Electrode Materials For Supercapacitors Operating With Electrolytes Containing Potassium Ions

by

Mengqi Zhou

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University

December, 2016
I am the author of the thesis entitled

Electrode Materials for Supercapacitors Operating With Electrolytes Containing Potassium Ions

submitted for the degree of Doctor of Philosophy

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: ..................................Mengqi Zhou......................................................
(Please Print)

Signed: ........ .................................................................

Date: .................................................................
I certify the following about the thesis entitled (10 word maximum)

Electrode Materials For Supercapacitors Operating With Electrolytes Containing Potassium Ions

submitted for the degree of Doctor of Philosophy

a. I am the creator of all or part of the whole work(s) (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.

b. The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

c. That if the work(s) have been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.

d. That any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

e. All research integrity requirements have been complied with.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: ........................................MENGQI ZHOU.........................................................
(Please Print)

Signed: ..............................................................

Signature Redacted by Library

Date: .................................................................
Acknowledgement

I would like to thank my principal supervisor Prof. Ying Chen for giving me a great opportunity to conduct frontier research work and finish my PhD course in the wonderful laboratories at Deakin University. I also appreciate my associate supervisor Dr. Alexey Glushenkov for helping me address fine details of my research project and being patient in revising this PhD thesis. I thank Dr. Olga Kartachova for helping me to start research work before I went deeply in my study and giving me a very good idea that assisted me in publishing my first journal paper during the PhD study.

I would like to thank Mr. Robert Lovett for helping me to access nanotechnology laboratories and training me on many instruments such as a glove box, vacuum ovens, the two-zone tube furnace and educating me in managing gases. I also appreciate Mr. Rob Pow for giving me GTP-Level 1 Induction to access many laboratories such as the thermal laboratory, electron microscopy and x-ray diffraction laboratories, and training me to conduct x-ray diffraction experiments to perform phase analysis. I thank Dr. Andrew Sullivan for training me on scanning electron microscopes and giving me many good suggestions to improve the quality of images of my samples. I also would like to thank Ms. Rosey Van Driel for training me on a transmission electron microscope and helping me to understand the fundamental
mechanism behind it deeply. I would like to thank Dr. Yuncang Li for helping me to
carry out the biocompatibility test for my first research work.

Finally, I would like to thank my group mates Dr. Tao Tao, Dr. Luhua Li, Dr.
Weiwei Lei, Dr. Dan Liu and Dr. Md Mokhlesur Rahman for helping me during my
experiments. I also thank Dr. Thrinathreddy Ramireddy and Dr. Tan Xing for their
advice required for a part of my research work. I thank Mr. Si Qin, Mr. Qiran Cai for
helping me in the laboratory and social life. Finally, I really appreciate my family for
supporting me to undertake my PhD course and live in Australia.
Journal Publications List

1. Results presented in Chapter 3 have been published in the article:


Abstract

Considering growing interest in developing green power sources, supercapacitors are the promising candidates due to their unique characteristics such as high power density, long cycling life, low cost and environment friendliness. Electrode materials and electrolytes are playing important roles in supercapacitors. Thus, high value supercapacitors require suitable electrode materials and matchable electrolyte; this important consideration is the focus of this thesis. In particular, many transition metal and carbon-based electrode nanomaterials operate at optimum conditions in potassium-based electrolytes, and the performance of various electrode materials is considered in this thesis.

Titanium dioxide nanotubes are synthesized via anodization method with subsequent annealing treatment at different temperatures and are evaluated in neutral potassium chloride (KCl) aqueous electrolyte. Two samples are selected to be investigated for their biocompatibility and also evaluated electrochemically in a physiological electrolyte, phosphate-buffered saline. The results of electrochemical testing demonstrate a high specific capacitance and good cycling stability for 1000 cycles. This work is suggested to lead to future developments in the area of implantable or wearable supercapacitors.

Furthermore, nanoporous vanadium and tungsten oxynitrides are produced by ammonia reduction method to study the volumetric capacitance in potassium hydroxide as an alkaline electrolyte. These electrode materials are promising for
devices with a smaller footprint because of their high density and, therefore, a relatively high volumetric capacitance. In this study, I evaluate two electrochemical cells for each material (a three-electrode cell and a symmetric two-electrode cell) in order to evaluate volumetric capacitance, cyclic stability and the performance of prototype symmetric supercapacitors.

Finally, a new type of hybrid capacitor, potassium-ion capacitor, is discussed in this thesis. Activated carbon and graphite are tested as prospective capacitive and battery-type electrode materials for this device. The commercial activated carbon (Kuraray YP-50F) optimized for supercapacitor application and commercial grade graphite are used for the study, and individual half-cells are assembled utilizing an organic electrolyte (KPF6 in EC/DEC (1:1)). In addition, suggestions for the design of a prototype full device of potassium-ion hybrid capacitor are given.
# Table of Contents

## Chapter 1: Introduction and literature review ..........................................1

1.1 Introduction .............................................................................................................1

1.1.1 Global challenges .................................................................................................1

1.1.2 Electrochemical energy storage devices and preference for nanostructured materials in supercapacitors .......................................................................................1

1.2 Research objectives .................................................................................................2

1.3 Critical literature review ..........................................................................................4

1.3.1 Principle of supercapacitors .................................................................................4

1.3.2 Applications of supercapacitors ........................................................................11

1.3.3 Electrode and electrolyte materials ....................................................................14

1.3.3.1 Carbon-based materials ................................................................................16

1.3.3.2 Transition metal oxides and nitrides .................................................................18

1.3.3.3 Conductive Polymers .....................................................................................23

1.3.3.4 Electrolytes ......................................................................................................24

1.4 Thesis structure .......................................................................................................25

## Chapter 2: Research methodologies .................................................................26

2.1 Synthesis methods .................................................................................................26

2.1.1 Temperature-programmed heating ........................................................................26

2.2 Analysis methods ....................................................................................................28

2.2.1 Thermogravimetrical analysis ............................................................................28

2.2.2 X-ray diffraction .................................................................................................28

2.2.3 Scanning electron microscopy ..........................................................................29

2.2.4 Low-temperature nitrogen adsorption ...................................................................30

2.2.5 Raman spectroscopy ..........................................................................................31

2.3 Electrochemical testing methods ...........................................................................33

2.3.1 Preparation of electrodes ....................................................................................33
2.3.1.1 Measurement cells for electrodes in aqueous electrolytes ........................................... 34
2.3.1.2 Measurement cells for electrodes in an organic electrolyte ........................................... 35
2.3.2 Electrochemical measurement methods ............................................................................. 36
  2.3.2.1 Cyclic voltammetry ........................................................................................................ 37
  2.3.2.2 Galvanostatic charge-discharge ................................................................................... 38
  2.3.2.3 Electrochemical impedance spectroscopy ...................................................................... 38

Chapter 3: Biocompatible titanium dioxide nanotube films for supercapacitors electrodes ................................................................. 41
  3.1 Introduction .......................................................................................................................... 41
  3.2 Experimental ..................................................................................................................... 42
  3.3 Results and discussion ...................................................................................................... 45
    3.3.1 Structural characterisation ......................................................................................... 45
    3.3.2 Electrochemical properties in KCl electrolyte .............................................................. 47
  3.4 Conclusions ....................................................................................................................... 52

Chapter 4: Volumetric capacitance of porous vanadium oxynitride and tungsten oxynitride supercapacitor electrodes ........................................... 54
  4.1 Introduction .......................................................................................................................... 54
  4.2 Experimental ..................................................................................................................... 58
  4.3 Results and discussion ...................................................................................................... 60
    4.3.1 Composition and morphology of nanoporous vanadium oxynitride and tungsten oxynitrides ..................................................................................................................... 60
    4.3.2 Electrochemical properties of nanoporous vanadium oxynitride and tungsten oxynitride in three-electrode systems ................................................................. 64
    4.3.3 Electrochemical properties of vanadium oxynitride and tungsten nitride in symmetric cells ..................................................................................................................... 69
  4.4 Conclusions ....................................................................................................................... 75
Chapter 5: Activated carbon and graphite electrode materials for hybrid K-ion capacitors: electrochemical tests of individual electrodes and suggestions for designing the full cell capacitor ...........................76

5.1 Introduction ........................................................................................................................................ 76

5.2 Experimental ..................................................................................................................................... 78

5.2.1 Preparation of electrodes and coin cells ......................................................................................... 78

5.2.2 Characterisation ................................................................................................................................. 79

5.3 Results and discussion ......................................................................................................................... 80

5.3.1 Evaluation of morphology and structure in the graphite and activated carbon electrode materials ......................................................................................................................... 80

5.3.2 Electrochemical properties of activated carbon and graphite in potassium half cells and suggestions for designing a full cell device ......................................................................................................................... 86

5.3.2.1 Half-cell performance of the activated carbon and graphite electrodes ................................. 86

5.3.2.2 Suggestions for the design of a full cell K-ion capacitor ......................................................... 89

5.4 Conclusions ......................................................................................................................................... 94

Chapter 6: Summary and future work .................................................................................................96

References ...............................................................................................................................................103
List of Figures and Tables

Figure 1.1 Ragone plot for various energy storage devices [11].................................5

Figure 1.2 Representation of a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell...6

Figure 1.3 Representation of a battery (Daniell cell) showing the key features of battery operation........................................................................................................................................7

Figure 1.4 Schematic representation of an operating principle of the highly reversible lithium-ion battery [14]................................................................................................................7

Figure 1.5 Representation of an electrochemical capacitor (supercapacitor), illustrating the energy storage in the electric double layers at the electrode-electrolyte interfaces. ...............................................................................................................................9

Figure 1.6 Schematic illustration of symmetric supercapacitors and asymmetric or hybrid supercapacitors [24]................................................................................................................11

Figure 1.7 The pore structures model of a carbon material........................................16

Figure 1.8 Schematic representation of hexagonal and rhombohedral graphite [35]. Units cell are highlighted as well .................................................................18

Figure 2.1 Two-zone furnace (Tetlow Kilns & Furnaces Pty Ltd, Australia)........27

Figure 2.2 Schematic diagram and fundamental principle of a scanning electron microscope. ..................................................................................................................30

Figure 2.3 Tristar 3000 nitrogen adsorption/desorption instrument........................31

Figure 2.4 Renishaw inVia Raman microscope. .........................................................33
Figure 2.5 A schematic representation of a three-electrode cell (left) and a two-electrode cell (right). .................................................................34

Figure 2.6 A schematic configuration of a hybrid full cell (with graphite and activated carbon electrodes) and a half cell (used for evaluation of individual electrodes). Coin-type cells are used in experiments.................................................................36

Figure 2.7 Solartron 1470E electrochemical workstation (a) and Land Battery Test System (b) .................................................................37

Figure 2.8 Example of an equivalent circuit used for fitting of the experimental data. R_e and R_ct are the electrolyte and charge transfer resistances, respectively, while CPE_{dl} and CPE_{W} are constant phase elements, used to represent the double layer capacitance and diffusion impedance for a porous material. ......................................................39

Figure 3.1 Anodization titanium dioxide nanotubes and annealing treatments. ......43

Figure 3.2 XRD patterns of the samples (NT-600, NT-650 and NT-700). ..............45

Figure 3.3 SEM images of the TiO_2 nanotube films: (a) NT-600, (b) NT-650, (c) NT-700. The inset shows a higher magnification image of the nanotube layer in NT-700. ........................................................................46

Figure 3.4 Electrochemical properties of NT-600, NT-650 and NT-700 in 3M KCl aqueous electrolyte: (a, b and c) cyclic voltammetry and galvanostatic chargedischarge curves of titanium dioxide nanotubes NT-600; (d, e and f) cyclic voltammetry and galvanostatic discharge-charge curves of NT-650; (g, h and i) cyclic voltammetry and galvanostatic discharge-charge curves of NT-700; (j)
electrochemical impedance spectra of the three samples; (k) enlarged view of the impedance spectra for NT-600 and NT-650; (l) the plot of capacitance as a function of current density for the three samples. .................................................................48

**Figure 3.5** Biocompatibility of NT-650: cell numbers after the contact with a TiO$_2$ nanotube film without annealing in Ar and the sample NT-650 obtained after annealing at 650°C. Cell numbers for the control experiment are also shown. All cell numbers were measured after 7 days of cell culturing..............................................50

**Figure 3.6** Electrochemical properties of NT-600 and NT-650 in 0.01 M PBS solution: (a, b and c) cyclic voltammetry and galvanostatic charge-discharge curves of NT-600; (d,e and f) cyclic voltammetry and galvanostatic charge-discharge curves of NT-650; (g) the plot of capacitance as a function of current density for the two samples; (h) the cyclic stabilities of the two samples.................................................................52

**Figure 4.1** X-ray diffraction patterns of vanadium oxynitride (a) and tungsten oxynitride (b).............................................................................................................60

**Figure 4.2** SEM images of nanoporous vanadium oxynitride; (a) low-magnification image and (b) high-magnification image. .................................................................62

**Figure 4.3** SEM images of nanoporous tungsten oxynitride; (a) low-magnification image and (b) high-magnification image .................................................................64

**Figure 4.4** Electrochemical properties of vanadium oxynitride in 3M KOH in a three-electrode system; (a) cyclic voltammetry test for the scan rates of 2 to 50 mV/s, (b) galvanostatic charging/discharging test for the current densities from 0.05 to 1 A/cm$^3$,
(c) electrochemical impedance spectroscopy test, and (d) specific volumetric capacitance calculated from the discharge part of the cycle. .............................................. 65

**Figure 4.5** Electrochemical properties of tungsten oxynitride in 3M KOH in a three-electrode cell. (a, b) cyclic voltammetry tests at scan rates between 2 and 500 mV/s, (c) galvanostatic charging/discharging tests for the current densities between 0.05 and 1 A/cm³, (c) electrochemical impedance spectroscopy test, and (d) plot of specific volumetric discharge capacitance vs current density. ................................................................. 68

**Figure 4.6** Electrochemical properties of vanadium oxynitride in 3M KOH in a symmetric cell. (a and b) cyclic voltammetry test for the scan rates varied between 2 mV/s to 2 V/s, (c and d) galvanostatic charging/discharging test for the current densities varied from 0.05 and 10 A/cm³, (e) electrochemical impedance spectroscopy test, and (f) the dependence of the specific volumetric discharge capacitance on the current density. ............................................................................. 70

**Figure 4.7** Electrochemical properties of tungsten oxynitride in 3M KOH in a symmetric cell. (a, b) cyclic voltammetry tests for the scan rates varied between 2 mV/s and 5 V/s, (c) galvanostatic charging/discharging tests for the current densities between 0.05 and 1 A/cm³, (d) electrochemical impedance spectroscopy test, and (e) specific volumetric discharge capacitance vs current density. .................................................. 73

**Figure 4.8** The cycling stabilities of symmetric capacitors with (a) vanadium oxynitride and (b) tungsten oxynitride at a current density of 0.5 A/cm³ in 3M KOH aqueous electrolyte. ......................................................................................................................... 74
Figure 5.1 SEM images of YP-50F activated carbon, depicting its morphology at low (a) and high (b) magnifications.

Figure 5.2 SEM images of commercial graphite, depicting its morphology at low (a) and high (b) magnifications.

Figure 5.3 Raman spectra of YP-50F activated carbon and commercial graphite.

Figure 5.4 Nitrogen adsorption/desorption isotherms of YP-50F activated carbon and commercial graphite.

Figure 5.5 Pore size distribution of activated carbon via BJH method.

Figure 5.6 Electrochemical properties of activated carbon in potassium half-cells: (a) the capacity and cyclic stability at a 50mA/g current density; (b) the capacity of activated carbon at a multi-current density 50 mA/g and 100 mA/g; (c) charge and discharge curves at 50 mA/g; (d) charge and discharge curves at 200mA/g.

Figure 5.7 Electrochemical properties of graphite in potassium half-cells: (a) the capacity and cyclic stability of graphite at a 25 mA/g current density; (b) the specific capacity of graphite at a multi-current density from 25 mA/g to 1 A/g; (c) charge and discharge curves at 25 mA/g; (d) charge and discharge curves at 200 mA/g.

Figure 5.8 Ideal charging and discharging curves in different potassium ion supercapacitors: (a) half-cell charging & discharging, (b) full-cell charging & discharging.

Figure 5.9 Schematic representation of pre-cycling routines for the graphite and activated carbon electrodes: (a, b) in a scenario in which both cathode and anode are pre-cycled; (c, d) in a scenario in which only anode is pre-cycled. The charge-
discharge curves and termination points for the graphite electrodes are shown in (a) and (d), and those for the activated carbon are shown in (b) and (c). Note that the cathode in (c) is not pre-cycled as used in the full cell directly as is. ........................................93

**Table 1.1** Comparison of some important characteristics of state of the art supercapacitors and lithium-ion batteries [25-27]..........................................................12

**Table 3.1** Sample Description.....................................................................................43

**Table 4.1** Estimated elemental composition of oxynitrides (the data are reproduced from ref. [118]).................................................................................................61

**Table 5.1** BET surface areas and parameters of porous structure for YP-50F activated carbon and commercial graphite. .................................................................85
Chapter 1: Introduction and literature review

1.1 Introduction

1.1.1 Global challenges

With the rapid development of the contemporary world, people rely heavily on the generation and consumption of energy. Fossil fuels, such as oil, gas and coal, have been indispensable energy sources in the last century and will be this century, at least for some time. The fossil fuels are clearly the main power source in the modern world (80% energy is derived from fossil fuels) [1]. However, the environment is being affected by the usage of fossil fuels, as greenhouse and toxic gases such as CO$_2$, CO, SO$_2$ and NO$_x$ are released. This leads to global warming and climate change [2-4]. Finding and using sustainable energy sources such as wind, solar, nuclear fusion and terrestrial heat, among others, are gaining attention of governments, enterprises and individuals. The clean energy from the renewable sources needs to be converted to electricity for the practical use. In this context, electrochemical energy storage devices are becoming an important research field to ensure the efficient use and management of electricity generated from renewable sources.

1.1.2 Electrochemical energy storage devices and preference for nanostructured materials in supercapacitors

Electrochemical energy storage devices are based on chemical reactions and physical processes to store electric energy in their electrode materials. They include secondary metal-ion batteries (e.g. lithium-ion battery), supercapacitors and fuel cells [5, 6]. There are not only differences between the three storage systems but also “electrochemical similarities” [7]. Both batteries and fuel cells rely on redox reactions between electrolytes and surfaces of electrodes. The principle of storage in most commercialised supercapacitors is based on ion
adsorption and desorption, although some electrode materials may also operate via surface redox reactions. This thesis is focused predominantly on electrode materials for supercapacitors, and these electrode materials are normally required to be nanostructured.

Nanostructured materials generally have building units with the size at a scale of a few nanometres. The nanoscale size (less than 100 nm) may be a particle’s diameter, grain size, thickness of a layer or width of a conducting line on an electronic chip [8]. Nanostructured materials and nanomaterials have numerous advantages. For instance, nanoparticles have high surface area and short diffusion lengths for the insertion of guest ions [9]. Due to their great physical and chemical properties, nanomaterials have started to play a very important role in electrochemical energy storage devices during recent decades. A critical advantage for the application is supercapacitors is the high surface area of nanomaterials. This important property enhances the contact area between electrolyte and the electrode’s surface and, therefore, leads to an electric double layer that can store more charge or more redox-active sites for surface redox reactions. Most of the electrode materials studied in this thesis (excluding graphite) can be classified as nanostructured materials.

1.2 Research objectives

The performance of various electrode materials may vary in different electrolytes. In particular, an active ion that underpins the charge storage mechanism may be of importance. In this thesis, I specifically study the performance of electrodes for electrochemical supercapacitors in electrolytes utilising potassium ions. An overview of possible advantages of potassium-based electrolytes is given in the section 1.3.3, while the main thesis objectives are given in this section. They include:
1. Produce certain types of transition metal oxides and oxynitrides with controlled nanostructures

The transition metal compounds have been identified as promising candidate electrode materials for supercapacitors due to their unique physical-chemical performances and low cost. A number of such materials, TiO$_2$, vanadium and tungsten oxynitrides, are the focus of work in this thesis. In particular, nanotubes of TiO$_2$ and nanoporous oxynitrides are evaluated. It is of interest to evaluate TiO$_2$ structures as it is believed that this material can be biocompatible and can be used for creating wearable or implantable supercapacitors. Nanoporous oxynitrides exhibit pseudocapacitive behaviour and it is expected that, due to their relatively high density, high volumetric capacitances can be achieved in these materials.

2. Investigate these electrode materials in potassium-containing electrolytes

Electrolytes with potassium ions will be focused on in this thesis due to their unique physical, chemical and biocompatible properties. To evaluate the performance of TiO$_2$ nanotube films, they are pre-tested in KCl aqueous electrolytes and subsequently assessed in a potassium-containing solution emulating a body fluid. Vanadium and molybdenum oxynitrides are assessed in an aqueous KOH electrolyte. Their performance in both three-electrode cells as well as symmetric cells is evaluated.

3. Investigate electrode materials for potassium-ion capacitors, a new type of supercapacitors with a non-aqueous electrolyte

Finally, graphite and activated carbon electrodes are evaluated for their potential application is a potassium-ion capacitor. This type of a capacitor is a hybrid cell in which a battery-type electrode is combined with a capacitive electrode. It is generally expected that a cell of this type may have an increased energy density while retaining the traditional
advantages of supercapacitors such as attractive power densities. Before a prototype of such a cell is practically demonstrated, individual electrodes need to be assessed separately and considerations for the assembly of a full cell device need to be analysed at a level of a conceptual study.

1.3 Critical literature review

1.3.1 Principle of supercapacitors

Electrochemical capacitors, also called supercapacitors, are a new type of electrical storage devices with characteristics intermediate between traditional capacitors and batteries [10]. In 1957, the first patent for an electrochemical capacitor was registered by Becher and the first of this kind of devices was produced by SOHIO in 1969 [11]. Despite supercapacitors having unique capabilities compared with other electrochemical storage devices, especially batteries and traditional capacitors, its energy density is lower than that of batteries and fuel cells, while power density is worse than that of traditional capacitors. Kotz presented the so called “Ragone plot” highlighting the specific energy and specific power (Figure 1.1) of various electrochemical storage devices. He also pointed out that the supercapacitors filled the gap between batteries and conventional capacitors such as electrolytic capacitors or metallized film capacitors [11]. It can be seen from Figure 1.1 that the area of supercapacitors does not only overlap with capacitors but also overlaps with batteries. It seems that supercapacitors can have specific power densities comparable to those of capacitors and specific energy densities as high as those of some types of batteries. However, to achieve more promising energy density and power density, supercapacitors still need to be improved. The key to this is improving fundamental understanding of the processes in supercapacitors and their electrode materials.
Although both batteries and fuel cells convert electrical energy via redox reactions, fuel cells use gas or liquid fuels from outside storage volumes. For example, hydrogen/oxygen fuel cells are using hydrogen gas to react with oxygen gas to produce electricity with by-products of water and heat as shown in Figure 1.2 [7, 12]. The following processes happen in this fuel cell:

Anode reaction: \( H_2 \rightarrow 2H^+ + 2e^- \)

Cathode reaction: \( \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \)

Overall reaction: \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \)

Figure 1.1 Ragone plot for various energy storage devices [11].
Unlike fuel cells, batteries are closed systems [7]. The active mass is in the electrodes (anode and cathode) themselves rather than outside. Let us consider the so-called Daniel cell as an example to explain the principle of battery’s operation. During the charging process, metal Cu oxides to Cu$^{2+}$ on the cathode and Zn$^{2+}$ reduces to metal Zn on the anode (Figure 1.3). It reverses on discharge. However, a part of this process is irreversible because of the losses in mass during charging and discharging. A new type of highly reversible battery has been reported during 1970s, which is the lithium-ion battery [13]. As a metal-ion battery, the lithium-ion battery has a different mechanism (“rocking chair”) and typically operates in a non-aqueous electrolyte, providing more energy and power density than traditional types of batteries. A schematic representation of the lithium-ion battery principle is shown in Figure 1.4 [14]. It can be seen that lithium ions de-intercalate from the cathode, move through the electrolyte and insert into the anode during charging process. The reverse process occurs during discharging, i.e. the intercalated lithium ions de-intercalate from the anode and intercalate into the cathode. The anode and cathode should be lithium host materials able to
accommodate the ions reversibly. Sodium-ion and potassium-ion batteries are new types of batteries similar to lithium-ion batteries.

---

**Figure 1.3** Representation of a battery (Daniell cell) showing the key features of battery operation.

**Figure 1.4** Schematic representation of an operating principle of the highly reversible lithium-ion battery [14].
The operation principle of supercapacitors is mainly based on absorption and desorption of ions on the electrolyte/electrode interfaces. That means that the energy storage mechanism is different from that in batteries. There are two storage ways in supercapacitors which are, respectively, Faradaic and non-Faradaic processes [10]. In more conventional supercapacitors (Figure 1.5), the negative electrode attracts cations of an electrolyte and the positive electrode attracts anions during the charging process, forming the so called electric double layers on both electrodes. The cations and anions will be released back to the electrolyte when the supercapacitors discharge. There is no transfer of charge across the electric double layer and, therefore, this mechanism represents a non-Faradaic process. The non-Faradaic supercapacitors are also called ‘double-layer capacitors’. The operation of double-layer capacitors can be illustrated by a simple circuit of two capacitors connected in series. The capacitance of each electric double layer can be expressed as

\[ C_{dl} = \frac{\varepsilon A}{t}, \]

where \( \varepsilon \) is the electrolyte dielectric constant, \( A \) is the true surface area (specific surface area) of the electrode, and \( t \) is the thickness of the electric double-layer [15]. According to this formula, if specific capacitance \( (C_{dl}) \) needs to be enhanced, specific surface area of the electrode material should be as high as possible and the charge separation should be extremely small. Activated porous carbon, for example, seems to have the biggest specific surface area in carbon-based materials due to their developed porous structure [16-19] and are commonly used in the commercialised electrochemical supercapacitors.
In addition, supercapacitors do not only include double-layer capacitors, but also pseudocapacitors. The principle of pseudocapacitors is similar to batteries because they are based on Faradaic redox reactions. Nevertheless, the localisation of redox reactions is different between batteries and pseudocapacitors. Most researchers propose that the redox reactions in pseudocapacitors occur at the surface and this provides high reversibility and speed during charging/discharging [15, 20-22]. One contributing process in a pseudocapacitive system may be chemisorption of ions or molecules described by the following equation:

$$M + A^- \leftrightarrow M/A^{(1-\delta)^-} + \delta e(in M).$$

The reaction at the surface of electrode M usually causes potential-dependent pseudocapacitance and the quality $\delta e$ is related to the so-called “electrosorption valence”
Chapter 1. Introduction and literature review

[10]. The pseudocapacitive process is able to contribute a greater amount of electrochemical energy storage, ten to hundred times more than the electric double-layer [23].

Furthermore, the full-cell supercapacitors are divided into two types: symmetric and asymmetric (hybrid) supercapacitors. The symmetric supercapacitors are assembled using two identical positive and negative electrodes which can be electrochemical double layer type electrodes or pseudoucapacitive electrodes (Figure 1.6a and b). In the cases of asymmetric supercapacitors, there are three types of devices shown in Figure 1.6 (c), (d), and (e). The first type of asymmetric supercapacitors can be assembled by combining an electric double layer (EDL) electrode and a pseudoucapacitive electrode. The second type of asymmetric supercapacitors can use an EDL electrode and a battery-type electrode. The last type of asymmetric supercapacitors is assembled by combining a pseudoucapacitive electrode and a battery-type electrode. In conventional literature, e.g. in the work by Zhang et al. [24], the carbon materials as EDL materials were only used as electrodes. However, there are alternative choices of electrode materials that can be utilised, e.g. TiO2, tungsten oxynitride. These materials will be introduced in the next section. Otherwise, electrolytes are also important components for ether symmetric or asymmetric supercapacitors. In symmetric systems, aqueous electrolytes, such as KCl, KOH, etc. can be used but the voltage range can be expanded if non-aqueous (organic) electrolytes are used.
Chapter 1. Introduction and literature review

1.3.2 Applications of supercapacitors

The applications of supercapacitors have been investigated since 1957 when the first supercapacitors were produced [11]. There are several advantages in supercapacitors compared with batteries. Table 1.1 shows directly the comparison of performances among lithium-ion batteries, supercapacitors and hybrid cells. As it can be seen, there is a huge difference of the electrochemical characters between electrochemical capacitor and battery technologies, and this situation is not predicted to change in the foreseeable future. The suitability of each technology for particular applications will remain markedly different.
regardless of likely advances that may be made in either of the technologies. Therefore, supercapacitors are able to be applied in applications requiring short time of charge/discharge and high power density and small electric storage devices such as engine start, seaport cranes, electric vehicles, power sources for artificial organs. Otherwise, hybrid cells, as the new generation energy storage devices, have been fill the gap between lithium ion batteries and supercapacitors due to the unique properties such as energy density exceeding that of supercapacitors and higher power density exceeding that of batteries. According to the parameters of hybrid cells in Table 1.1, they can be utilised in collecting wasted energy in equipment and vehicles. Some important applications are overviewed in more detail next.

Table 1.1 Comparison of some important characteristics of state of the art supercapacitors and lithium-ion batteries [25-27].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>State of the art lithium-ion battery</th>
<th>Supercapacitor</th>
<th>Hybrid cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Charge time</td>
<td>~3-5 minutes</td>
<td>~1 second</td>
<td>~12 second</td>
</tr>
<tr>
<td>*Discharge time</td>
<td>~3-5 minutes</td>
<td>~1 second</td>
<td>~12 second</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&lt;5000 @ 1C rate</td>
<td>&gt;500000</td>
<td>&gt;9000 @ 120 C</td>
</tr>
<tr>
<td>Specific energy</td>
<td>70-100</td>
<td>5</td>
<td>30-70</td>
</tr>
<tr>
<td>(Wh/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific power</td>
<td>**0.5-1</td>
<td>5-10</td>
<td>0.1-6</td>
</tr>
<tr>
<td>(kW/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle efficiency</td>
<td>70-85</td>
<td>~100</td>
<td>85-98</td>
</tr>
<tr>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost/Wh</td>
<td>$1-2/Wh</td>
<td>$10-20/Wh</td>
<td>N/A</td>
</tr>
<tr>
<td>Cost/kW</td>
<td>$75-150/kW</td>
<td>$25-50/kW</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Time for discharge and charge of the useable total energy stored in the devices.

** Power capability of the battery for short duration partial discharge at 90% efficiency.
1. Electric vehicles

In 1859 Wakefield immersed the assembly into a container bearing dilute sulfuric acid and developed the first lead-acid battery [28]. Since 1993, the first idea of modern hybrid battery vehicles was reported by Ovshinsky who suggested nickel metal battery as a power source of vehicles [29]. The research in electric vehicles has been conducted for more than two decades. Electric vehicles can run on batteries, supercapacitors, fuel cells or their combination with conventional combustion engines (hybrid vehicles) [30]. Supercapacitors could not be used in vehicles as a sole power source until the past decade due to the lower capacities than those of batteries and fuel cells. The electric energy is provided mainly by batteries for vehicles. However, the cycle life of batteries is lower than that of supercapacitors, which leads to a higher running cost of electric vehicles due to the need to replace batteries frequently. In order to deal with this issue, high energy density supercapacitors have been researched. In 2008, the first shuttle bus using supercapacitors appeared in Shanghai World Expo to support travel of visitors in every exhibition hall. The chargers of the electrochemical capacitor were in every bus stop so that the bus could be recharged. This is a milestone in the application of vehicles with supercapacitors as a new type of electric vehicles.

2. Biomedical applications

With the progress of medical technology, various biomedical devices have been developed such as artificial joints, biosensors or heart pacemakers. Some of these devices
use power sources, most commonly batteries. There are, however, several drawbacks of using batteries in the human body:

1. Batteries have long charge times. For example, an implantable sensor produced by Telemetry Research Ltd requires 4 hours to charge [31].

2. Batteries cannot have long cycle life. This means that alternative power sources with longer cycle life need to be considered.

3. Most of the electrode or electrolyte materials of batteries are toxic for human body. Once the batteries leak, the patients have life-threatening conditions.

Thus, biocompatible supercapacitors may meet these requirements. Microsupercapacitor, for instance, has been designed by Abidin in 2011 [32]. This device consists of silicon substrate, polymer-coated nickel electrodes and gel polyvinyl alcohol as the electrolyte. The maximum capacitance was 0.061pF. In addition, Hur et al. designed a DNA hydrogel-based supercapacitors operating in the environment of body fluids [33]. DNA hydrogel (D-gel) as the electrode was performing well in a human body and the electrolyte was close in composition to human body fluids, physiological environment. However, the assembling process is very complex and there are doubts that it can be apply at a large scale. Overall, biocompatible supercapacitors have just started being developed in the last few years. There are several issues that need to be solved, including identifying biocompatible materials, increasing life-time of the electrode and evaluating potential toxicity.

1.3.3 Electrode and electrolyte materials

An assembled electrochemical capacitor or hybrid cell consists mainly of two electrodes, electrolyte and separator, which can be seen in Figure 1.5 and Figure 1.6. The electrodes and electrolyte play very important roles in these energy storage devices. Because the mechanism of electrochemical energy storage of supercapacitors is chemical or physical
reactions on the interface of the electrode and the electrolyte, electrodes are of a particular importance. Furthermore, in the case of hybrid cells, there are not only interface-based chemical or physical reactions, but also bulk redox reactions in one of the electrodes typical for metal-ion batteries. Electrolytes are able to facilitate greatly the performance of electrodes in various cell configurations. Therefore, finding a good match between electrode materials and different types of electrolytes is very important. The performance of a number of electrode materials in potassium-containing electrolytes is addressed specifically in this thesis.

Electrode materials can be divided into three main categories - carbon-based, transition metal oxides/nitrides and conductive polymers [34]. They adsorb or insert ions on one side of materials and connect to a current collector on the opposite side to collect or supply electrons needed for redox activity. An ideal combination of properties for all of the electrode materials in supercapacitors are high capacitance or capacity, long cycling life, high rate of conduction and physicochemical stability in the environment of the cell [10]. However, following deep materials research, the issues of electrode materials have been identified by many experts. For example, carbon-based materials, such as activated porous carbon, have lower capacitance than another two types of electrode materials. Conductive polymers materials are considered to have higher impedance than carbon-based materials. Moreover, other problems, such as self-discharge, electrolyte matching or working temperature are estimated to impact the performance of supercapacitors. As a consequence of this, there is an existing need for further research and development of supercapacitor electrode materials.
1.3.3.1 Carbon-based materials

The family of carbon-based materials includes porous activated carbons, carbon nanotubes, carbon nanorods, carbon nanowires, graphite, graphene and carbon aerogels [16-19, 35]. The best benefit of carbon-based materials in supercapacitors is their easily achievable high surface area originated from an enriched porous structure. Porous materials can be divided into three types, which are, respectively, microporous (<2 nm), mesoporous (2 to 50 nm) and macroporous (>50 nm) forms. The same material may have a hierarchical structure of pores, e.g. a combination of macropores, mesopores and micropores, such as a configuration shown in Figure 1.7 [36].

*Figure 1.7 The pore structures model of a carbon material.*
It is clear that porous activated carbon materials have the highest surface area (2650 m²/g), and, therefore, this type of materials is able to obtain the highest capacitance among various carbon materials. An important aspect of the performance of activated carbons is that a certain part of surface area may be not accessible for the electrolyte due to the mismatch between the pore size and size of (solvated or desolvated) ions, leading to a value of capacitance smaller than the theoretical one. The optimisation of supercapacitors involving activated carbon materials includes optimisation of both pore design of carbon electrode and also the molecular dimensions of the electrolyte and the solvent [37]. For example, Eliad et al. [37] have highlighted a good match between pores of 4.2Å in a model material with the size of K⁺ and Cs⁺ ions (3.62-4.2Å). Accordingly, the ions are able to be absorbed in the corresponding pores on the surface of the porous carbon material and the surface area of the electrodes can be utilised at a reasonable level during the process of charging. In contrast, the pores with sizes smaller than the size of ions were insufficient, leading to the decrease in the demonstrated capacitance. Therefore, both high surface area and an appropriate porous structure are important for an optimal electrode material.

Unlike activated carbon, graphite materials have usually much lower surface areas and a different internal structure as they consist of well-stacked graphitic planes. The structure of graphite is formed by multiple-layer carbon atoms sheets. Graphite belongs to sp² bonding type in the family of carbon materials, with hexagonal atomic arrangement in each carbon sheet [35]. It may exist in the form of two types of atom layer ordering such as hexagonal graphite (ABAB layer stacking) and rhombohedral graphite (ABCABC layer stacking), as shown in Figure 1.8 [38]. The storage in graphite electrodes is typically dominated by ion intercalation rather than the formation of an electric double layer. In an event when intercalation is prevented, only small capacitances of up to 12 F/g have been
observed by Gomibuchi due to the low specific surface area [39]. Due to the dominating intercalation mechanism, graphite is utilized in hybrid capacitors in organic electrolytes, especially in activated carbon/graphite hybrid cells, as a battery-type electrode [40-45].

![Hexagonal graphite and Rhombohedral graphite](image)

*Figure 1.8 Schematic representation of hexagonal and rhombohedral graphite [35]. Units cell are highlighted as well.*

### 1.3.3.2 Transition metal oxides and nitrides

In addition to carbon materials, transition metal oxides and nitrides are intensively researched, including RuO$_2$, NiO$_2$, MnO$_2$, TiO$_2$, V$_2$O$_5$, TiN and VN materials. They often have greater capacitances than those of carbon-based materials. However, these materials also suffer from a few unique drawbacks.

**1) Ruthenium oxides (RuO$_2$)**

A noble metal oxide, RuO$_2$ has been focused on by many researchers due to its highest capacitance [10, 46-49]. The capacitance of RuO$_2$ electrode is contributed by reversible Faradaic redox reactions. The principle reactions are showed as:

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x \quad 0 \leq x \leq 2 \quad (1)$$
and

\[ RuO_x(OH)_y + \delta H^+ + \delta e^- \rightleftharpoons RuO_{x-\delta}(OH)_{y+\delta} \]  

Accordingly, in acidic electrolytes, electrons and ions can be transferred fast on the surface of RuO₂, with an electrosorption of protons following a Frumkin-type isotherm [34]. The capacitance was considered to be more than 700 F/g, the highest in transition metal oxides [50]. However, there are still several disadvantages of RuO₂. As mentioned before, RuO₂ is a noble metal oxide. That means this type electrode material is really expensive, which is not practical.

(2) Manganese oxides (MnOₓ)

Manganese oxide (MnOₓ) is a well-researched type of electrode materials for supercapacitors because of the low cost of raw materials and its ideal electrochemical behaviour. As electrode materials for supercapacitors, manganese oxides include the following phases: MnO₂ (Mn⁴⁺), Mn₂O₃ (Mn³⁺) and Mn₃O₄ (Mn²⁺, Mn¹⁺). The capacitance of MnOₓ is contributed by double layer storage behaviour and also by insertion of protons and ions. Manganese oxides with high surface area have been the research points as the surface area can facilitate both types of storage mechanisms. High capacitances can be achieved. For example, porous MnO₂ has been reported to have a high capacitance of 261 F/g in 0.5M K₂SO₄ electrolyte [51]. The pseudocapacitive contribution to the capacitance is provided in two processes:

\[ MnO_2 + H^+ + e^- \rightleftharpoons MnOOH \]

and

\[ MnO_2 + C^+ + e^- \rightleftharpoons MnOC \]
\[(\text{MnO}_2)_{\text{surface}} + C^+ + e^- \rightleftharpoons (\text{MnO}_2^{-}C^+)_{\text{surface}}\]

where \(C^+ = \text{Na}^+, \text{K}^+, \text{Li}^+\) [52].

The mechanism can be slightly different in \(\text{Mn}_3\text{O}_4\), another important variety of manganese oxides. The capacitance of \(\text{Mn}_3\text{O}_4\) can be as high as 420 F/g in aqueous KCl electrolyte, and around 82% remains of this capacitance remains after 400 cycles [53]. The partial capacitance was contributed by pseudocapacitance reaction

\[\text{MnO}_x(\text{OH})_y + \delta H^+ + \delta e^- \rightleftharpoons \text{MnO}_{x-\delta}(\text{OH})_{y+\delta}\]

where \(\text{MnO}_x(\text{OH})_y\) and \(\text{MnO}_{x-\delta}(\text{OH})_{y+\delta}\) stand for the oxymanganese species under the higher and lower oxidation states, respectively [53]. Manganese oxides have several disadvantages such as instability during long term cycles and high impedance during redox reaction.

(3) Iron oxide (Fe\(_3\)O\(_4\))

Iron oxide (Fe\(_3\)O\(_4\)) is another recently discovered inexpensive electrode material. This electrode material is considered to have the capacitance only slightly lower than that of RuO\(_2\). The highest capacitance was reported to be 510 F/g in Na\(_2\)SO\(_4\) with a wide potential window of 1.2 V [54]. This behaviour is suggested to originate from a different capacitance mechanism than that of either RuO\(_2\) or MnO\(_2\). Wang et al. [55] have investigated the capacitance mechanisms of an Fe\(_3\)O\(_4\) capacitor in Na\(_2\)SO\(_3\), Na\(_2\)SO\(_4\), and KOH aqueous solutions by various analysis methods. MFe\(_2\)O\(_4\) (M = Mn, Fe, Co, or Ni), similar crystal structures to Fe\(_3\)O\(_4\), have been studied by Kuo et al. [56]. The capacitance of MnFe\(_2\)O\(_4\) as a pseudocapacitive electrode material decreases by 18% during the first 1000 cycles and then
remains unchanged throughout 3000 cycles. The good cyclability may have to do with very small volume variations.

(4) Titanium oxides (TiO₂) and titanium nitrides (TiN)

TiO₂ is also a novel candidate electrode material for supercapacitors due to its great physical-chemical stabilities, easy control of the structure, accessible surface area for solvated ions, high conductivity and low cost [57-69]. The electrochemical energy storage principle of this material is double layer capacitive behaviour[70]. Generally speaking, capacitance of TiO₂ is around 10-40 μF/cm² due to the electrochemical storage process. However, the capacitance of nanostructured TiO₂ can be be up to 90 to 120 μF/cm² [71]. In addition, different phase structure and morphological character influence electrochemical performance of titanium oxide. Films of titania nanotube arrays can be excellent electrode materials because of high surface area [64, 67, 70, 72, 73]. Moreover, the nature of the TiO₂ phase is also a crucial parameter of TiO₂. Titanium oxide exists in the form of 12 polymorphs which are respectively rutile (tetragonal, P42/mnm), anatase (tetragonal, I41/amd) and brookite (orthorhombic, Pbca), TiO₂-B, TiO₂-H, TiO₂-R, TiO₂-II (α-PbO₂-like), baddeleyite, TiO₂-OI, TiO₂-OII, cubic form and fluorite. Electrochemical properties of these phases have been studied in the past decades [68, 74]. In supercapacitors, there is no significant changes of capacitance among rutile, anatase and brookite phases [75]. Nevertheless, orthorhombic structure of brookite TiO₂ is complex and is difficult to prepare [68]. Rutile phase of TiO₂ has a higher conductivity and lower charge transfer limitations compared with anatase [76]. The morphological architecture can, however, have a higher influence than the nature of the phase. Finally, titanium nitride (TiN) is paid attention very recently due to its greater conductivity. The mechanism of TiN electrochemical storage is double layer behaviour and
pseudocapacitance occurring by the chemisorptions of cations/anions, with capacitances of up to 238 F/g [77].

(5) Vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) and vanadium nitride (VN)

Vanadium-based materials are great potential candidates for electrodes in supercapacitors, particularly vanadium oxides and nitride. The capacitance of vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) can be up to 262 F/g in 2M NaCl aqueous solution [78]. The disadvantage of V\textsubscript{2}O\textsubscript{5} is its low conductivity. In order to address this issue, carbon-based materials were added to V\textsubscript{2}O\textsubscript{5} to improve cycling life, and up to 80% of capacitance was retained after 10,000 cycles [79]. Furthermore, vanadium nitride is the newest high-performance electrode material of supercapacitors. It has been reported that the capacitance of porous nanocrystalline VN is the highest of transition metal based materials (up to 1340 F/g in 1M KOH aqueous electrolyte) [80, 81]. The capacitance of VN (or vanadium oxynitride) is contributed by pseudocapacitive behavior which is shown below,

\[
\text{VN}_x\text{O}_y + \text{OH}^- \rightleftharpoons \text{VN}_x\text{O}_y//\text{OH}^-,
\]

where \(\text{VN}_x\text{O}_y//\text{OH}^-\) represents adsorption of hydroxide ions at specific sites on the oxynitride surface induced by ion-dipole attraction [80]. In addition, the structures of VN is also a crucial parameter for electrochemical properties. Glushenkov et al. have reported the behaviour of the porous nanocrystalline VN in supercapacitors [82]. This article shows that the fine-tuning of both the crystalline structure of the nitride and the surface composition of the oxygen-containing layer is important for the creation of an efficient nanostructured VN material for supercapacitors. In reality, it is common for transition metal nitrides to contain some oxygen as it is difficult to synthesize pure nitride. For this reason, it is more appropriate
(6) Other transition metal oxides and nitrides

Some of transition metal oxides and nitrides that have not been mentioned include tungsten, molybdenum, and tungsten molybdenum oxynitrides [83-87]. They are also good alternative electrode materials for supercapacitors with high capacitances, long cycle life and high conductivity.

1.3.3.3 Conductive Polymers

As the electrode materials with Faradaic pseudocapacitive behaviour, conductive polymers are attracting attention for the application in supercapacitors due to their fast and reversible redox reactions [88, 89]. The Faradaic pseudocapacitive process between polymers and electrolytes is also called doping process and these electrode materials become electronically conductive after the charge-transfer process [90]. For example, in polythiophene p- and n-doping/undoping processes happen as shown below:

\[
\left( \begin{array}{c}
\text{S}
\end{array} \right) \ n + nyA^- \xrightleftharpoons{p\text{-doping}}^{undoping} \left( \begin{array}{c}
\text{S}
\end{array} \right)^{+y} \ A^-yn + nye^-
\]

\[
\left( \begin{array}{c}
\text{S}
\end{array} \right) \ n + nye^- + nyc^+ \xrightleftharpoons{n\text{-doping}}^{undoping} \left( \begin{array}{c}
\text{S}
\end{array} \right)^{-y} \ c^-yn
\]

where \(C^+\) and \(A^-\) are ions from electrolytes. According to the scheme, the charging/discharging process is considered an insertion/deinsertion process. Thus, conductive polymers may also be described as ion-insertion electrode materials. In addition,
it is believed that p-dopable polymers are more stable against degradation than n-dopable polymers [91]. Therefore, investigations of the p-doping polymers are pursued by researchers. Additionally, conductive polymers still possess higher resistance compared with carbon-based materials and transition metal oxides. Preparing composites with highly conductive materials, such as carbon nanotubes, is a good choice to enhance electrochemical properties of conductive polymers [27].

1.3.3.4 Electrolytes

An electrolyte is another important component of a capacitor. Generally, they can be divided into liquid electrolytes (aqueous and non-aqueous) and solid state electrolytes. Aqueous electrolytes can commonly be acidic, alkaline and neutral. For example, KCl and KOH aqueous electrolytes are used in this thesis.

Neutral electrolytes with K\(^+\) ions (for instance, KCl) have a higher ion mobility than electrolytes with other common ions such as Li\(^+\) or Na\(^+\). As a result, a better electrochemical performance can be obtained, e.g. during a cyclic voltammetry test [52]. KCl salt can also be found in body fluids, which means that these liquids may possibly be used with biocompatible electrodes in many fields. Secondly, K\(^+\) in alkaline electrolytes has also a higher conductivity than in acid electrolytes. KOH, as an ideal aqueous electrolyte, can be suited to particular electrode materials such as vanadium oxides or nitrides [82, 92]. Finally, organic electrolytes containing potassium ions have a somewhat higher ion mobility (than lithium- and sodium-containing electrolytes) and a larger operational potential window may be achieved in potassium-ion batteries and capacitors than that in lithium-ion and sodium-ion cells. Some battery-type electrode materials (e.g., graphite and Sn) can work in the potassium ion containing organic electrolytes and exhibit high capacities. These benefits of
potassium electrolytes can lead to new devices, e.g. hybrid potassium-ion capacitor analyzed in this thesis.

1.4 Thesis structure

This thesis is divided into six chapters presenting different aspects of the work within the wider research question. Chapter 1 defines the research context and contains a review of the existing literature on the principles of different energy storage devices with an emphasis on supercapacitors and hybrid capacitor as well as their applications. This chapter also highlights the electrode materials and electrolytes for supercapacitors and hybrid capacitors. Chapter 2 briefly summarizes experimental methodologies used to synthesize, characterize and test materials in supercapacitors and hybrid cells. Chapters 3-5 contain experimental results and their discussion. Chapter 3 is focused on titanium dioxide nanotubes with different phases working in neutral electrolytes (potassium chloride) and the biocompatible application in a body fluid containing potassium ions. In Chapter 4, electrochemical properties of the vanadium and tungsten oxynitrides are tested in an alkaline potassium hydroxide electrolyte in three-electrode and symmetric systems. Chapter 5 is focused on investigating the electrochemical properties of activated carbon and graphite in non-aqueous electrolyte. The results and discussion of these two materials in half cells have been presented in this chapter. Design and discussion of a hypothetical full cell are introduced for the first time. Chapter 6 contains conclusions and possible directions for future work.
Chapter 2: Research methodologies

This chapter is divided into three sections to introduce synthesis methods, analysis methods and electrochemical testing methods. The detailed experimental information related to specific experiments will be presented in the following chapters as well when required.

2.1 Synthesis methods

2.1.1 Temperature-programmed heating

The temperature-programmed heating method is one of the synthesis methods used in this thesis for the preparation of materials. This method can be used for oxidation reaction, reduction reaction or phase transformations and can be conducted in a furnace (such as a tube furnace, muffle furnace or vacuum furnace) that has a programmable temperature controller. In my work I have applied this method to the phase transformation reaction and ammonia reduction reaction, and the experiments were conducted in a tube furnace. A two-zone furnace (Tetlow Kilns & Furnaces Pty Ltd, Australia) was used for all temperature-programmed heat treatment experiments in this thesis and is shown in Figure 2.1.
One application of the temperature-programmed heating method is inducing phase transformations. For example, samples of TiO$_2$ nanotubes corresponding to the anatase phase of titania can be loaded into furnace and heated, under argon gas protection, to up to 700 °C. The anatase phase converts to the rutile phase completely after such a treatment, and this ensures a specific kind of the electrochemical performance of the material. More specific experimental details of this procedure are presented in the next chapter. In addition, the temperature-programmed heating method is also a better way to conduct ammonia reduction reaction of oxides to yield vanadium and tungsten oxynitrides. The ammonia as the reaction gas is supplied into the furnace tube to react with V$_2$O$_5$ or WO$_3$ powders to produce the corresponding oxynitrides. During the reaction, a porous structure can be produced in the materials. The temperature-programmed ammonia reduction procedure is described in more detail in Chapter 4.
2.2 Analysis methods

2.2.1 Thermogravimetical analysis

Thermogravimetical analysis (TGA) is an analysis method directed at monitoring mass changes in a material as a function of the changes in temperature. The information obtained from this method can be an evidence of the phase composition of materials at different temperatures. For example, a piece of titanium metal may be heated from room temperature to 800 °C to analyse the oxidation reaction of titanium in air. The TGA test in my project was carried out by a VETZSCH STA 409 PC TGA instrument. The highest temperature is within the range of 800-1200 °C. Two samples with the same weights are placed into two crucibles for analysis.

2.2.2 X-ray diffraction

X-ray diffraction (XRD) is used to determine the chemical composition, crystal structure, crystallographic orientation, and crystallite sizes. It is a non-destructive technique based on the interference of x-ray waves scattered along certain directions. The XRD measurement was taken with the help of a PANalytical X’Pert Pro instrument using Cu Kα radiation source (λ= 1.54181 Å) and operated at 40 kV and 30 mA current. The scan rate and step angle used for the measurements were 2 s/step and 0.02°, and a range of 20-100° was used for the measurement. The X’Pert data collection software was used to analyse and process the recorded data. The samples for the XRD analysis were prepared in the form of pellets of 13 mm diameter by pressing powders under 8 tonnes of load using an automatic pellet making instrument. Alternatively, thin film samples were analysed without modification. In this thesis, XRD is carried on for the analysis of different phases of TiO₂ films to establish the presence of anatase and rutile phases. In addition, the phases of
vanadium and tungsten oxynitrides as well as those of graphite and activated carbon were confirmed by the XRD results.

2.2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is used to study the morphology of nanomaterials. A beam of electrons with energy of 3-20 kV ejects secondary electrons, backscattered electrons, and x-rays from the surface of the sample when it interacts with the specimen. Surface topography is obtained from the ejected secondary electrons, and secondary electron imaging is a routine technique for the visualisation of the morphology of materials. Surface morphology was evaluated with the help of a Supra 55Vp FE-SEM instrument. The structure and fundamental principle of a scanning electron microscope is shown in Figure 2.2. In this thesis, scanning electron microscopy is used to observe the nanoscale morphology such as that of TiO₂ nanotubes, porous vanadium oxynitride and activated carbon.
2.2.4 Low-temperature nitrogen adsorption

The textural characteristics (surface area and pore size distribution) are very important parameters for electrode materials such as activated carbon. Low-temperature nitrogen adsorption/desorption is the common way to measure the textural parameters, and the adsorption/desorption isotherms can be used for the calculation of pore volume and pore size distribution. Nitrogen adsorption measurement of materials was conducted using a Tristar 3000 Micrometrics analyser and Brunauer-Emmett-Teller (BET) method. The samples are typically loaded into glass tubes and samples are degassed using N₂ gas at 150°
to remove air absorbed on the surface before the measurement. Subsequently, low-temperature nitrogen adsorption is conducted by exposing samples to varied levels of nitrogen pressure at cryogenic temperature. The surface area is calculated from the adsorption isotherm using 5-point BET method. The weight of the sample is controlled to be between 0.3 and 0.5 g. This method was used in this thesis for determining the specific surface area and pore size distribution of various samples.

![Figure 2.3 Tristar 3000 nitrogen adsorption/desorption instrument.](image)

2.2.5 Raman spectroscopy

Raman spectroscopy is useful for the identification of chemical compounds and phases from the vibrations of chemical bonds and symmetry. In this technique, a ray of monochromatic light, usually produced by a laser, interacts with the material and experiences two types of scattering, namely elastic and inelastic. The vibrational state of the material gets
excited from the ground state to a virtual, or excited, state by absorption of the incident light for a short duration and returns back to the original ground state by emitting a photon with energy equal to that of the incident photon. This is called elastic scattering or Rayleigh scattering. A vibration state of the material also gets excited from the ground state to an excited state on absorption of an incident photon and then returns to a different energy state by emitting a photon with an energy different from that of the incident photon. This is called inelastic scattering. There are two types of inelastic scattering. A vibration state of the material gets excited from the ground energy state to the virtual state and scatters back to the final vibrational energy state, higher in energy than the initial state, is called Stokes Raman scattering. If a vibration state of the material gets excited from the ground energy state to the virtual state and scatters back to the energy state, lower in energy than the initial state, the scattering is called anti-Stokes Raman scattering which is higher in energy. This is the fundamental process behind the Raman spectroscopy based on the Stokes Raman scattering. The shift in the frequency is measured in terms of wavenumber (cm\(^{-1}\)). The bonds that are sensitive to Raman spectroscopy occur only at particular wavenumbers, and from this fingerprint we can detect the structure of the material [186]. In this thesis, Raman spectroscopy of activated carbon and commercial graphite was conducted using a Renishaw inVia micro-Raman system, which is shown in Figure 2.4.
Chapter 2. Research methodologies

2.3 Electrochemical testing methods

2.3.1 Preparation of electrodes

In order to prepare an electrode, active materials are mixed with electronic conductor (carbon black) and binders (polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) powder or carboxymethyl cellulose (CMC) powder) in a suitable solvent (e.g., N-methyl-2-pyrrolidone (NMP) for PVDF, de-ionized water for CMC). A suitable ratio of components is followed. For example, the weight ratio of 8 : 1 : 1 of vanadium oxynitride, PTFE and carbon black was used in this work for vanadium oxynitride electrodes. The slurries are coated on metal plates, discs or foils, as appropriate to make electrodes, and those are typically dried in an oven to evaporate the solvents. Some electrode materials such as anodised TiO₂ nanotubes are used for electrochemical test directly, without conductors and binders. The TiO₂ nanotubes are supported on a Ti plate, which can be used as a current collector. More specific electrode preparation details are given in the experimental chapters.
2.3.1.1 Measurement cells for electrodes in aqueous electrolytes

In order to test supercapacitor electrodes in aqueous electrolytes, two typical measurement systems for evaluating electrochemical performance may be used. These are a three-electrode cell and a symmetric two-electrode cell. The three-electrode system includes a working electrode (prepared using an active material of interest), a counter electrode and a reference electrode. The counter electrode in this thesis is a Pt wire or mesh. The reference electrode in aqueous solutions can be either a Ag/AgCl electrode (for neutral or acidic electrolytes) or a Hg/HgO electrode (for basic electrolytes). The three-electrode system is shown schematically in Figure 2.5 (left). The two-electrode system may be used for evaluating symmetric supercapacitors. Two identical working electrodes are assembled together with a separator in between (such a cell is shown schematically in Figure 2.5 (right)).

![Figure 2.5 A schematic representation of a three-electrode cell (left) and a two-electrode cell (right).](image-url)
In each experiment, the components of the cells (including working electrode(s) in a PTFE holder) were placed into a beaker, and the beaker was subsequently filled with electrolyte under vacuum and outgassed for 10-15 min to infiltrate the electrolyte properly into the working electrode.

2.3.1.2 Measurement cells for electrodes in an organic electrolyte

The cells for evaluating electrodes in an organic electrolyte were prepared in a different way. Coin-type cells were used for experiments, and the cell types were full cells (in which hypothetical anode and cathode materials were placed together) and half-cells (in which a working electrode and a counter/reference potassium metal electrode were used). The full-cell system is a realistic prototype capacitor cell which involves a positive electrode and a negative electrode in the same manner they are used in a real device. In my work, graphite was coated on a copper foil to be used as the anode and activated carbon was coated on an aluminium foil to be used as the cathode. In contrast, a half-cell system is assembled by sandwiching working electrodes with a negative reference electrode in the form of a potassium plate. Both graphite and activated carbon were initially tested individually in a half-cell configuration. A schematic representation of both full-cell and half-cell configurations assembled in coin-type cells is given in Figure 2.6.
2.3.2 Electrochemical measurement methods

Most electrochemical tests were carried out on the electrochemical workstation Solartron 1470E, including cyclic voltammetry, electrochemical impedance spectroscopy and high current density galvanostatic charge-discharge tests. The instrument is shown in Figure 2.7 a. Some galvanostatic charge-discharge experiments (aimed, in particular, at assessing cyclabilities) were conducted on a Land battery test system, shown in Figure 2.7 b.
2.3.2.1 Cyclic voltammetry

Cyclic voltammetry is an important and versatile technique that can be used to explain the mechanisms occurring in the supercapacitor electrodes during charge and discharge. Cyclic voltammetry applies a linear ramp potential within a fixed potential window, and then changes the direction of the scan to the opposite to reach the original potential point. As a result, triangular voltage profile is applied to a cell. The current flowing in the cell under test is simultaneously measured. Peaks appearing in the cyclic voltammetry curve indicate the presence of redox reactions at particular potentials. The current recorded in the test can be due to two types of processes such as Faradaic and non-Faradaic processes. The oxidation and reduction processes are correlated with the charge transfer at the electrode’s interface. A non-Faradaic process is due to the electrical double layer formation at the electrode surface. The arrangement of the positive and negative charges at the electrode’s interface establishes the electric double layer and causes the difference in potential between electrode and electrolyte. The typical potential windows for tests of electrodes in aqueous electrolytes are between 1 and 1.2 V. If the potential window is larger than 1.2 V, water decomposes in most cases, which may lead to the failure of supercapacitors.
2.3.2.2 Galvanostatic charge-discharge

Galvanostatic charge-discharge (also commonly known as chronopotentiometry) is based on applying a constant current to the cell and studying the potential’s transient behaviour within a fixed potential window. This method is often used to measure the charge and discharge capacities and capacitances of supercapacitors. The charge capacity can be calculated using the formula

\[ Q \text{ (charge)} = I \Delta t, \]

where \( Q \) is the capacity (A·s), \( I \) is the current density (A) and \( \Delta t \) is time (s) required for the electrode to reach the cut off potential. The capacities are also commonly expressed in other units such as mAh and, for the evaluation of the electrode materials, specific values (per g of a material of interest) are often used.

For a full cell capacitor with a conventional triangular profile, energy density can be calculated from a chronopotentiometry measurement using the formula

\[ \text{Specific energy (Wh/Kg)} = \text{Charge} \times \text{voltage}/2 \]

2.3.2.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is based on evaluating the electrical response of a cell to an AC stimulation at various frequencies. In an electrochemical system, several phenomena occur as a response to an AC voltage input. They include electron transport towards the electrode/electrolyte interface through a conductor, double-layer charging or charge transfer reactions. These processes occur with different time constants and impedance spectroscopy enables extraction and analysis of useful data separately. When the electrochemical system, which could be modelled with an equivalent circuit containing elements such as resistors, capacitors or inductors, is stimulated with an AC voltage input,
the current response, as a result, will present a phase shift, dependent on the ratio of these elements. If \( V(t) = V_A \sin(\omega t) \) is the applied voltage with a frequency \( f \), where \( \omega = 2\pi f \), and the response current signal is \( I(t) = I_A \sin(\omega t + \varphi) \), where \( \varphi \) is the phase shift, then the impedance \( Z \) could be expressed in the following form:

\[
Z = \frac{V(t)}{I(t)} = \frac{V_A \sin(\omega t)}{I_A \sin(\omega t + \varphi)} = Z_A \frac{\sin(\omega t)}{\sin(\omega t + \varphi)}
\]

This expression could also be written using Euler’s formula \( \exp(j\varphi) = \cos(\varphi) + j \sin(\varphi) \) as a complex function with a combination of “real” and “imaginary” parts:

\[
Z = Z_A(\cos(\varphi) + j \sin(\varphi)) = Z_{\text{real}} + jZ_{\text{im}}
\]

In this thesis, electrochemical impedance spectroscopy is used to compare the intrinsic properties of oxynitrides applied as supercapacitor electrode materials, as frequency-response behaviour is affected by the characteristics of the analysed materials. Impedance measurements are performed with a Solartron electrochemical analyser operating
in a frequency range between 10 kHz and 0.01 Hz in a symmetric cell configuration at an open circuit potential. Fitting of the data is performed with ZView software.
Chapter 3: Biocompatible titanium dioxide nanotube films for supercapacitors electrodes

3.1 Introduction

TiO₂ is an interesting electrode material for the state-of-the-art electrochemical energy storage systems and can be used both in lithium-ion batteries [93-95] and electrochemical supercapacitors [94]. Films of TiO₂ nanotube arrays have particularly attracted attention for the application in supercapacitors because of their high surface area and have been a subject of a number of studies [57, 70, 73, 76, 96-105]. Based on the ideal capacitive response of TiO₂ (rectangular cyclic voltammetry curves) observed in some cases, researchers have previously assigned the storage mechanism in TiO₂ nanotube electrodes predominantly to the conventional electric double layer storage (see, for example, [76, 98]). Due to the low conductivity of TiO₂ and the amorphous nature of the anodized nanotubes, the capacitance of the pristine, as-anodized layer of TiO₂ nanotubes is quite low and, therefore, a number of approaches have been developed to improve the capacitance and rate capability of TiO₂ nanotube arrays via post-synthesis treatment and modification of its electronic conductivity, Ti³⁺/Ti⁴⁺ ratio, hydrogenation and induction of oxygen vacancies. For example, annealing in Ar atmosphere, [70, 73, 76, 101] thermal treatment in H₂ atmosphere, [57, 96] annealing in NH₃ atmosphere, [97] cathodic biasing of TiO₂ in an ethylene glycolelectrolyte, [99] second anodization with post-annealing in vacuum, [106] electrochemical hydrogenation or plasma-treatment, [102, 103] and cathodic polarization treatment [104, 105]. Capacitances between 1 and 20 mF/cm² have been commonly reported after conducting these additional treatments.

New emerging applications of electrochemical supercapacitors include ECs as power sources for implantable and wearable devices (such as, for example, pacemakers, implanted chips, sensors, smart power bodysuits) [107, 108]. For such applications it is advantageous
to use biocompatible electrode materials and other components of supercapacitors. It is also beneficial to shift from conventional electrolytes (often corrosive) to the electrolyte resembling physiological fluids [107]. It is also important to note that inorganic electrode materials in implantable or wearable supercapacitors have an advantage of possibly higher volumetric energy and power densities, and therefore may be preferred to carbon materials.

In this chapter, biocompatibility and the possibility of operation in a physiological-type electrolyte are investigated for the anodized films of titanium dioxide nanotubes post-annealed in Ar atmosphere. The phase composition and morphology of the nanotubes are assessed. Their encouraging electrochemical performance in neutral aqueous electrolytes (such as 3M KCl) as well as in a phosphate-buffered saline is presented. The phosphate-buffered saline is a common buffer solution used in biological research, non-toxic for cells (the consequences of leakage of such an electrolyte from a wearable or implantable device would be dramatically milder than for the leakage of conventional electrolytes). It is shown that the nanotube films have a suitable capacitive behavior in that type of electrolyte. The results of the biocompatibility test of the TiO$_2$ nanotube films are also reported.

### 3.2 Experimental

Titanium foils (purity of 99.7%) were used for anodization, which was performed in accordance with the procedure outlined elsewhere [109]. A two-electrode electrochemical system was used at room temperature. The electrolyte was a mixture of glycerol, 0.5 wt% NH$_4$F and 20 vol% H$_2$O. A Ti foil was used as a working electrode in each anodization experiment and a Pt foil was used as a counter electrode. The two electrodes were separated by a distance of 30 mm. A direct current power supply was used to control the voltage. The titanium foils were anodized at 30 V for 2 h to produce films of TiO$_2$ nanotubes on Ti foils. Three nanotube samples were subsequently annealed at 600°C, 650°C and 700°C in Ar
atmosphere for one hour. The synthesis procedure was shown in Figure 3.1 and three types of samples used in the tests are described in Table 3.1.

![Figure 3.1 Anodization titanium dioxide nanotubes and annealing treatments.](image)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT-600</td>
<td>Anodized nanotubes annealed at 600°C for one hour in Ar atmosphere</td>
</tr>
<tr>
<td>NT-650</td>
<td>Anodized nanotubes annealed at 650°C for one hour in Ar atmosphere</td>
</tr>
<tr>
<td>NT-700</td>
<td>Anodized nanotubes annealed at 700°C for one hour in Ar atmosphere</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD, PANalytical X-pert Pro MRD XL with Cu Ka radiation (λ = 1.5418 Å)) was used to analyze the phase composition of the samples. The scan rate and step angle used for the measurements were 2s/step and 0.02°, respectively, and the measurements were performed over a range of 2θ from 20° to 50°. The HighScore Plus v.3.0x software (PANalytical B.V. Almelo, The Netherlands) was used to analyse the recorded data. The surface morphology of titanium dioxide nanotubes was observed by scanning electron microscopy (SEM, Carl Zeiss SUPRA 55VP instrument).
The electrochemical properties were measured in the three-electrode cell including a working electrode (TiO₂ nanotubes on Ti foil), a counter electrode (Pt wire) and a reference electrode (Ag/AgCl). The cells were filled with 3 M KCl solution or 0.01 M phosphate-buffered saline (PBS, pH 7.4, Sigma-Aldrich) solution under vacuum. The electrochemical properties were characterized by galvanostatic charge-discharge and cyclic voltammetry (CV) measurements using a Solartron Analytical 1470E instrument. The potential window between -0.1 and 0.6 V vs Ag/AgCl was used in tests. The CV plots were recorded at scan rates from 1 to 500 mV/s. Galvanostatic charge-discharge curves were recorded at various current densities between 1.5 to 10 μA/cm² (per square cm of Ti substrate). The electrochemical impedance spectroscopy (EIS) was performed at the open circuit potential (OCP) within a frequency range from 100 kHz to 0.01 Hz using an Ivium-n-stat electrochemical analyser. The amplitude of the modulation signal was set to 5 mV. Experimental data were fitted with ZView v.3.1 software (Scribner Associates, Inc., UK).

The biocompatibility of all samples was evaluated using Osteoblast-like cells (SaOs-2, Sarcoma osteogenic) (Barwon Biomedical Research, Geelong Hospital, Victoria, Australia), a human osteosarcoma cell line [110, 111]. All samples for cell culture were sterilized in a muffle furnace at 180°C for 1 h. The samples were placed in a well in a 24-well cell culture plate. SaOs-2 cells were seeded on the surface of samples and the control without any sample at a cell density of 5 × 10³ cells per well. MTS assay was used to measure the in vitro proliferation of the SaOs-2 cells after cell culture for 7 days. The control is considered as biocompatible. In all cases, one-way analysis of variance was employed to evaluate the significant difference in the data, and the statistical difference was thought to be significant at p < 0.05.
3.3 Results and discussion

3.3.1 Structural characterisation

The XRD patterns of TiO$_2$ nanotube films annealed at 600, 650 and 700°C for one hour, which are shown in Figure 3.2. As it can be seen in Figure 3.2, XRD patterns of all samples have main peaks that match either rutile or anatase phases of TiO$_2$. The peaks located at 25.3°, 36.9°, 37.8°, 38.5° and 48° match the standard diffraction file of the anatase TiO$_2$ phase (# 01-070-7348); the peaks located at 27.4°, 36°, 39.1°, 41.2° and 44° match the standard diffraction file of the rutile TiO$_2$ phase (# 01-072-1148); finally, the peak at 40.1° matches the strongest peak of the Ti phase (Powder Diffraction File # 03-065-6231). It can be seen that the increase in annealing temperature leads to the formation of larger amounts of the rutile phase in the samples because more of the anatase phase transforms to the more stable rutile phase at higher temperatures. At 700°C, the anatase phase almost disappears and the pattern is dominated by the peaks of rutile TiO$_2$.

![Figure 3.2 XRD patterns of the samples (NT-600, NT-650 and NT-700).](image-url)
According to the SEM images in Figure 3.3(a), 2(b), 2(c), the typical morphologies of structures in the TiO₂ films on Ti can be observed. Arrays of nanotubes can be seen for each sample. The morphology changes after annealing at a higher temperature, and the nanotubes form bundles with increased gaps between the bundles. An enlarged SEM image of the sample NT-700 is shown in the inset of Figure 3.3 (c). It can be concluded the microstructure of the film changes when the annealing temperature is increased.

*Figure 3.3 SEM images of the TiO₂ nanotube films: (a) NT-600, (b) NT-650, (c) NT-700. The inset shows a higher magnification image of the nanotube layer in NT-700.*


3.3.2 Electrochemical properties in KCl electrolyte

The electrochemical properties of the three samples of nanotube films (NT-600, NT-650 & NT-700) in 3 M KCl aqueous electrolyte are shown in Figure 3.4. It can be seen in Figure 3.4(a), 3.4(d), 3.4(g) that the cyclic voltammetry (CV) curves of the three samples recorded at slow scan rates (in the range between 1 and 20 mV/s) in a three-electrode system have an ideal rectangular shape, mirror-symmetric in respect to the horizontal axis. The CV curves of NT-600 and NT-650 remain close to ideal and mirror-symmetric at higher scan rates (50 to 500 mV/s), as shown in Figure 3.4 b, e. In contrast, the CV curves of the sample NT-700 become elliptical at high scan rates (100 to 500 mV/s), as it can be seen in Figure 3.4(h). It appears that the sample NT-700 deviates from the ideal capacitive behavior at high scan rates.

The galvanostatic charge-discharge curves of the three samples recorded at various current densities (1.5, 2, 5 and 10 μA/cm\(^2\)) are shown in Figure 3.4(c), 3.4(f), 3.4(i). The shapes of all charge-discharge curves for the three samples are almost ideally triangular. The capacitances per unit of the electrode surface of NT-600, NT-650 and NT-700 can be calculated from the formula:

\[
C = \frac{I \cdot \Delta t}{V},
\]

where \(C\) is the capacitance per unit of the electrode surface (μF/cm\(^2\)), \(I\) is the current density per unit of the electrode surface (μA/cm\(^2\)), \(\Delta t\) is the time of discharge (s), and \(V\) is the potential window (V). The capacitances of NT-600 and NT-650 can be up to 1700 μF/cm\(^2\) and 1360 μF/cm\(^2\), respectively, at a current density of 1.5 μA/cm\(^2\). The sample NT-700 shows a sharply lower capacitance of only 620 μF/cm\(^2\) at the same low current density.
Chapter 3. Biocompatible titanium dioxide nanotube films for supercapacitors electrodes

Figure 3.4 Electrochemical properties of NT-600, NT-650 and NT-700 in 3M KCl aqueous electrolyte: (a, b and c) cyclic voltammetry and galvanostatic chargedischarge curves of titanium dioxide nanotubes NT-600; (d, e and f) cyclic voltammetry and galvanostatic discharge-charge curves of NT-650; (g, h and i) cyclic voltammetry and galvanostatic discharge-charge curves of NT-700; (j) electrochemical impedance spectra of the three samples; (k) enlarged view of the impedance spectra for NT-600 and NT-650; (l) the plot of capacitance as a function of current density for the three samples.

The electronic conductivities of the three samples were evaluated by electrochemical impedance spectroscopy, and the Nyquist plots are shown in Figure 3.4(j). The semi-circle area of plots for NT-600 and NT-650 is enlarged in Figure 3.4(k). The diameter of the semi-circle corresponds to the so called charge-transfer resistance at the electrode- electrolyte
interface, which is often correlated with the electronic conductivity of an electrode. The semi-circle diameters for the samples NT-600 and NT-650 are quite small and are around 20-25 Ohms for both. The semi-circle diameter of NT-700 is much higher and can be estimated to be about 2500 Ohms. This is likely to be correlated with the structural damage in the nanotube films at higher annealing temperatures (700°C), resulting in the sharply lower electronic conductivity of the sample. This is consistent with a much lower value of capacitance that can be calculated from the CV and charge-discharge curves of the sample NT-700. We conclude that the sample NT-700 has overall an inferior electrochemical performance to the other two samples and focus on the performance of NT-600 and NT-650 in the remainder of the study.

The plots of capacitance as a function of current density for the three samples are shown in Figure 3.4I. The capacitance of NT-600 drops to about 1015 μF/cm² at a high current density of 10 μA/cm². A 30% drop in capacitance of NT-650 is observed at the same high current density for the sample NT-650. Surprisingly, the capacitance retention in the NT-700 was probably the best despite the somewhat compromised structural integrity of this sample. The measured capacitance was, however, significantly lower than that of NT-600 and NT-650.

The measured electrochemical capacitances are generally in line with the values observed in the literature (1-20 mF/cm²) [57, 70, 73, 76, 96-99, 101-106]. Our values are close to the bottom of the range. The higher values of capacitance can be obtained when the samples are subjected to additional treatments such as annealing in Ar atmosphere [70, 73, 76, 101], thermal treatment in H₂ atmosphere [57, 96], annealing in NH₃ atmosphere [97], cathodic biasing of TiO₂ in an ethylene glycol electrolyte [99], second anodization with post-annealing in vacuum [106], electrochemical hydrogenation or plasma-treatment [102, 103], and cathodic polarization treatment [104, 105]. Optimization of the electrochemical
performance is, however, be-yond the scope of this paper. Instead, we focus in the rest of the manuscript on biocompatibility of the TiO$_2$ nanotube films and the possibility of their operation in electrolytes based on physiological liquids.

A biocompatibility assessment was carried out using an in-vitro cell culture for the sample of TiO$_2$ nanotubes before and after heat-treatment in Ar at 650°C while the empty well with cells was used as the control group. The cell numbers after cell culturing for 7 days are shown in Figure 3.5. It can be seen that the cell numbers on the sample before the heat-treatment was similar to that of the control. The cell numbers on the sample after the heat-treatment was higher than that of the control. It indicates that TiO$_2$ nanotubes before and after annealing are biocompatible and the heat-treatment increases the biocompatibility of the sample.

![Biocompatibility](image)

*Figure 3.5 Biocompatibility of NT-650: cell numbers after the contact with a TiO$_2$ nanotube film without annealing in Ar and the sample NT-650 obtained after annealing at 650°C. Cell numbers for the control experiment are also shown. All cell numbers were measured after 7 days of cell culturing.*
Figure 3.6 shows the electrochemical performance of NT-600 and NT-650 electrodes in 0.01 M PBS solution. The nanotube electrodes are characterized by CV and galvanostatic charge-discharge. The CV curves of NT-600 and NT-650 are close to the ideal, rectangular shapes at low scan rates (Figure 3.6a, d). Elliptical shape appears in the CV curves at very high scan rates (500 mV/s), indicating that the limitations of the transport phenomena are more pronounced in the three-electrode cell with 0.01 M PBS electrolyte in respect to the cell with the conventional 1 M KCl aqueous electrolytes. It can be concluded from the CV measurement that anodized titanium dioxide nanotubes after annealing are capable of displaying capacitive properties in the physiological electrolytes.

Charge-discharge curves confirm these findings, showing approximately triangular curves (Figure 3.6c, f). The measured capacitance of NT-600 is 1040 μF/cm² at a low current density (1.5 μA/cm²) and over 60% of capacitance can be preserved high current density (10 μA/cm²). Interestingly, the capacitance of NT-650 can be up to 2817 μF/cm², which is much higher than that of NT-600. We can assume that the mixture of rutile and anatase phases is capable to have higher capacitance than the single anatase phase in the PBS solution. However, this type of material cannot be stable during long cycling as shown in Figure 3.6h. Indeed, the NT-600 sample has a noticeably better stability after 1000 cycles although its capacitance is limited to only 640 μF/cm² at a current density of 10 μA/cm². In summary, it has been confirmed that the TiO₂ nanotubes demonstrate biocompatible behavior while, at the same time, being capable of operating in a physiological liquid. We expect that these results will promote further research in this area.
Figure 3.6 Electrochemical properties of NT-600 and NT-650 in 0.01 M PBS solution: (a, b and c) cyclic voltammetry and galvanostatic charge-discharge curves of NT-600; (d, e and f) cyclic voltammetry and galvanostatic charge-discharge curves of NT-650; (g) the plot of capacitance as a function of current density for the two samples; (h) the cyclic stabilities of the two samples.

3.4 Conclusions

The films of titanium dioxide nanotubes were produced by anodization and were annealed at various temperatures (600, 650 and 700°C). The XRD results indicate that the produced films of TiO₂ nanotubes contain anatase and rutile phases. The contribution of the anatase phase decreases with the increase of the annealing temperature, and the rutile phase is dominant in the material annealed at 700°C. The SEM analysis confirms the morphology of nanotubes and indicates changes at higher annealing temperatures, where the structural integrity of the nanotubes declines and nanotubes tend to aggregate into bundles. In line with
previous reports, the nanotube films possess capacitive properties, but the capacitance drops noticeably at a higher annealing temperature (700°C).

To conduct preliminary evaluation of TiO$_2$ nanotube electrodes for possible applications in implantable and wearable supercapacitors, a biocompatibility test and electrochemical characterization in a physiological liquid (0.01 M PBS solution) were conducted. It is shown that the nanotube films show biocompatible behavior, with the number of cells in contact with the material increasing over time. Nearly ideal capacitive behavior of TiO$_2$ nanotube films can be demonstrated in a physiological liquid. The specific capacitance of 1040 $\mu$F/cm$^2$ is recorded for the nanotube film annealed at 600°C while the sample is also capable of demonstrating a stable cyclic behavior.
Chapter 4: Volumetric capacitance of porous vanadium oxynitride and tungsten oxynitride supercapacitor electrodes

4.1 Introduction

As a different type of materials, transition metal oxides have been considered as alternatives to carbon electrode materials for supercapacitors. For example, RuO$_2$ has been reported as one of the highest capacitance materials for supercapacitors. Zheng et al. have shown that capacitance of a RuO$_2$·$x$H$_2$O electrode can be up to 768 F/g in 0.5 M H$_2$SO$_4$ electrolyte [112]. However, the Ru-based materials have high cost. Therefore, many researchers are focusing on other oxides. In particular, another type of oxides that has also been attracting researchers for the last 10-20 years is manganese oxides (MnO$_2$ and Mn$_3$O$_4$). The experimentally observed capacitance of MnO$_2$ is lower than that of RuO$_2$ and is around 150 F/g, according to Brousse et al. [113]. The main mechanism of these materials relies on the redox reactions which lead to high capacitances but poorer stability, because these reactions may cause mass loss or irreversible reaction side products in the electrodes. For this reason, new electrode materials such as transition metal nitrides and oxynitrides can be used as replacement for oxides as they have different physical and chemical properties. For example, transition metal nitrides have higher conductivity than that of conventional transition metal oxides, because the formation of transition metal nitrides modifies...
the nature of d-bond for the parent metal which causes the d-band to center nearer to
the Fermi energy level [114]. This feature of structures and bonding endows transition
metal nitrides with attractive electronic conductivity, catalytic activity and optical
properties [115]. The electrochemical stabilities of transition metal nitrides and
oxynitrides are often better than those of pure oxides. Most of transition metal oxides
have Faradaic pseudocapacitive behaviour in aqueous electrolytes (acid, basic or
neutral ones). Transition metal oxynitrides, such as titanium oxynitride, vanadium
oxynitride, tungsten oxynitride or molybdenum oxynitride, have high chemical
resistance and enhanced stabilities in corrosive electrolytes, such as aqueous KOH
[116, 117]. Based on these unique properties, transition metal oxynitrides are
promising candidate electrode materials of electrochemical supercapacitors.

Vanadium oxynitride is cheaper than RuO₂ and has higher capacitance in a
supercapacitor electrode than those of other transition metal oxynitrides (e.g.,
tungsten oxynitride or molybdenum oxynitride). This is because vanadium oxynitride
has a large operational potential window (1.2 V) and a combination of
electrochemical double layer capacitance and Faradaic pseudocapacitance [34].
Vanadium oxynitride works in KOH electrolyte within 1.2 V potential range with
high specific capacitance of 186 F/g [82]. In addition, Choi et al. [81] have reported
that vanadium oxynitride prepared via ammonia VCl₄ method has extremely high
pseudocapacitance of around 1300 F/g (this result is however somewhat controversial;
other researchers are typically able to measure lower capacities of 150-300 F/g). For tungsten oxynitride, the storage mechanism is electrochemical double layer capacitive behaviour in KOH aqueous electrolyte as considered by many researchers [85, 86, 118]. Tungsten oxynitride produced by Choi via the ammonia reduction method has been found to have the specific capacitance of around 30 F/g at 2 mV/s scan rate [119]. Using a similar production method, Ko et al. have prepared W$_2$N with capacitances of up to 100 F/g at 50 mV/s scan rate [120]. Both electrode materials have the same storage mechanism in aqueous KOH electrolyte, but the results are different. This can be a consequence of the influence of the phase of tungsten oxynitride on the electrochemical properties.

Compared to carbon-based electrode materials, vanadium oxynitride or tungsten nitride still has lower stable gravimetric capacitances. Normally, vanadium oxynitride and tungsten oxynitride have a capacitance around 50-200 F/g in alkaline electrolytes. At the same time, carbon-based materials have higher capacitances of 100-400 F/g [16]. This is partially because carbon-based materials have natural advantages, for instance, they have a lower density while activated carbons also have higher specific surface areas than those of most transition metal-based materials. However, some of the transition metal-based materials have higher volumetric capacitance than those of carbons. For example, Ti$_3$C$_2$T$_x$ clay has a high volumetric capacitance of 900 F/cm$^3$ and is stable in 1M H$_2$SO$_4$ electrolyte for over 10 thousand
cycles during charge and discharge, as reported by Ghidiu et al. [121]. At the device level, cells with vanadium oxynitride may have a higher volumetric energy density than that of cells with carbon electrodes. For example, Lu et al. [122] have presented that the volumetric energy density of VO\textsubscript{x}//VN asymmetric devices is up to 0.61 mWh/cm\textsuperscript{3}. The energy density of symmetric graphene-based supercapacitors and symmetric carbon nanotube-based supercapacitors have been reported to be 0.06 mWh/cm\textsuperscript{3} and 0.02 mWh/cm\textsuperscript{3}, respectively. Recognising the importance of volumetric values, more and more researchers have started reporting the results of volumetric energy density for their supercapacitor cells. Therefore, the volumetric capacitance and energy density are very important metrics for electrode materials of supercapacitors. Unfortunately, there is no any report for volumetric capacitances of tungsten oxynitride, W(O,N), and vanadium oxynitride, V(O,N), while these materials are quite heavy, with large density. It is important to study them for supercapacitor application where the size or footprint of the energy storage device is important.

In this chapter, I prepare nanoporous vanadium oxynitride and tungsten oxynitride via ammonia reduction method and measure their volumetric capacitances as electrode materials. The compounds are also characterised by X-ray diffraction and SEM to understand their composition and morphology. Electrochemical performance is tested in the three-electrode and two-electrode symmetric systems.
The volumetric characteristics of vanadium oxynitride and tungsten oxynitride can be concluded from the experimental results.

### 4.2 Experimental

Porous vanadium and tungsten oxynitrides were produced, respectively, from commercial vanadium pentoxide (V$_2$O$_5$) and tungsten trioxide (WO$_3$) powders (Sigma-Aldrich Australia, purity $\geq$98%) by temperature-programmed ammonia reduction method. 600 mg of vanadium pentoxide (or tungsten trioxide) powder were loaded in an alumina combustion boat and heated in a tube furnace up to the temperature of 700°C with a temperature increase rate of 180°C/h. The final temperature was kept for 1h. The ammonia gas was supplied into furnace for 30 min before starting heating and the ammonia flow rate was 0.7 L/min during the whole annealing procedure. After annealing, the passivating gas with set composition (Argon with 0.02 vol.% O$_2$) was supplied into the furnace for 45min. This process introduces a controlled oxygen-containing layer on the surface of oxynitrides and prevents burning of samples in air.

The electrodes were prepared as follows: 85 wt.% of vanadium oxynitride (tungsten oxynitride) powder were mixed with 10 wt.% of carbon black and 5 wt.% of PTFE (in the form of 60 wt.% PTFE suspension in water). The mixture of electrode components was loaded into a beaker with 50 mL of ethanol and then stirred for 4h at 60°C. After that, the gel-like slurry was ground in a mortar until it was nearly dried.
and rolled with a pin. The pre-formed electrodes were sandwiched between two Celgard separators and passed through a rolling press machine to compact the electrodes further. Finally, the electrodes were dried at 80°C in a vacuum oven overnight. As-prepared electrodes were stored in an Ar-filled glove box. The electrodes were cut into 1x1 cm² squares and evaluated. The thickness of the electrodes was measured by Vernier caliper. The thickness of vanadium oxynitride electrode was 0.275 mm and the weight was 23 mg, while the thickness of tungsten oxynitride was 0.24 mm and its weight was 20 mg. In order to investigate the electrochemical properties, the thick vanadium oxynitride (tungsten oxynitride) electrodes were tested in both symmetric systems and three-electrode systems with a Hg/HgO electrode as a reference electrode and a Pt wire as a counter electrode in 3M KOH electrolyte. The symmetric cells were assembled into sandwich-type devices, which are presented in Chapter 2. Cyclic voltammetry and galvanostatic charge/discharge methods were applied for characterisation of vanadium oxynitride (tungsten oxynitride) volumetric electrochemical behaviours in the alkaline electrolyte. The operating potential window of both methods was from -1.1 V to 0.1 V in the three-electrode system and from 0 to 1.2 V in symmetric system. The scan rates of the CV method were varied between 1 and 500 mV/s. The current density of the CD method was varied between 5 and 10 A/cm³. The electrochemical impedance spectroscopy was also used for the analysis of electrodes.
4.3 Results and discussion

4.3.1 Composition and morphology of nanoporous vanadium oxynitride and tungsten oxynitrides

![X-ray diffraction patterns of vanadium oxynitride (a) and tungsten oxynitride (b).](image)

*Figure 4.1 X-ray diffraction patterns of vanadium oxynitride (a) and tungsten oxynitride (b).*
In order to investigate the phase and elemental composition of the two electrode materials, XRD and WDS techniques were applied. The phase identification of vanadium oxynitride and tungsten oxynitride was performed by X-ray diffraction, and the results are shown in Figure 4.1. The elemental compositions of the electrode materials were measured previously by WDS and the results in Table 4.1 are reproduced from ref. [118]. As it can be seen in the XRD patterns, vanadium oxynitride peaks (Figure 4.1 a) match the positions of either VN or VO phases (their crystalline structures are identical, and it is difficult to distinguish between them by peak positions alone). Six peaks of tungsten oxynitride are located at 30.1°, 37.5°, 43.7°, 63.4°, 76.1° and 80.1° and match the phases of W₃N₄ (PDF # 75-1002) and W₀.₇₅(O,N) (PDF # 25-1255). According the WDS results (Table 4.1), the materials are indeed oxynitrides and both oxygen and nitrogen are present. Oxygen and nitrogen atomic percentages in vanadium oxynitride are 43.7% and 14.8%, respectively. Tungsten oxynitride contains respectively 39.9 at.% of nitrogen.

<table>
<thead>
<tr>
<th>Metal (at.%)</th>
<th>Nitrogen (at.%)</th>
<th>Oxygen (at.%)</th>
<th>M/(N,O) ratio</th>
<th>O/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(N,O)</td>
<td>41.7</td>
<td>43.7</td>
<td>14.8</td>
<td>0.7</td>
</tr>
<tr>
<td>W(N,O)</td>
<td>35.6</td>
<td>39.9</td>
<td>24.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
chemical element and 24.2 at.% of oxygen element, respectively. Consequently, the compositions of the two samples can be expressed as $V_{0.7}(N,O)$ and $W_{0.6}(N,O)$.

![SEM images of nanoporous vanadium oxynitride](image)

*Figure 4.2 SEM images of nanoporous vanadium oxynitride; (a) low-magnification image and (b) higher-magnification image.*
The morphologies of vanadium and tungsten oxynitrides are characterised by SEM, and the images are presented in Figure 4.1 and Figure 4.2. As it can be seen in Figure 4.1(a), micro-scale particles can be observed. It is obvious that the porous structure is formed after the temperature-programmed NH$_3$ treatment. This can be easily seen in the largest particle in the center of the SEM image, which has a large surface with numerous holes. This particle is further magnified in Figure 4.1(b). The pore sizes are mostly below 150 nm, and it can be concluded that the NH$_3$ reduction of V$_2$O$_5$ particles leads to the development of porosity at a high temperature [82]. Similar to vanadium oxynitride, tungsten oxynitride particles also display a strongly nanoporous structure, which can be seen in Figure 4.2. A low magnification image of the powder of tungsten oxynitride prepared from a commercially available WO$_3$ powder can be observed in Figure 4.2(a). Small pores with sizes of 20 nm and below are visible on the tungsten oxynitride particles in Figure 4.2(b). In summary, nanoporous structures of vanadium and tungsten oxynitrdes can be successfully produced through the temperature-programmed NH$_3$ reduction method at high temperature (700°C).
Chapter 4. Volumetric capacitance of porous vanadium & tungsten oxynitride supercapacitor electrodes

4.3.2 Electrochemical properties of nanoporous vanadium oxynitride and tungsten oxynitride in three-electrode systems

Vanadium and tungsten oxynitrides have better electrochemical performances and chemical stabilities in alkaline aqueous electrolytes, as it is mentioned in previous sections. Therefore, the volumetric capacitance tests of the two materials were performed in 3M KOH aqueous electrolyte.
Chapter 4. Volumetric capacitance of porous vanadium & tungsten oxynitride supercapacitor electrodes

Figure 4.4 Electrochemical properties of vanadium oxynitride in 3M KOH in a three-electrode system; (a) cyclic voltammetry test for the scan rates of 2 to 50 mV/s, (b) galvanostatic charging/discharging test for the current densities from 0.05 to 1 A/cm$^2$, (c) electrochemical impedance spectroscopy test, and (d) specific volumetric capacitance calculated from the discharge part of the cycle.
Figure 4.4 shows the results of testing a vanadium oxynitride electrode cyclic voltammetry (between scan rates of 2 to 50 mV/s), galvanostatic charge-discharge (at currents varied between 0.05 and 1 A/cm$^3$) and electrochemical impedance spectroscopy. The dependence of volumetric capacitance on current density is plotted in Figure 4.4(e). It can be seen from Figure 4.4(a) that the shapes of CV curves at low scan rates are asymmetric and non-rectangular, with obvious redox reaction peaks. The main oxidation peak and main reduction peak are respectively formed at -0.57 V and -0.98 V. Due to the presence of the redox peaks, it is likely that vanadium oxynitride has Faradaic pseudocapacitive behaviour during charging and discharging in KOH solution. According to Kumta et al. [77], this pseudocapacitive behaviour may originate from the OH$^-$ group’s reactions with VO$_x$ and VN$_x$ phases at different charge or discharge potentials, and a reaction of the following type

$$\text{VN}_x\text{O}_y + \text{OH}^- \leftrightarrow \text{VN}_x\text{O}_y||\text{OH}^- + \text{VN}_x\text{O}_y - \text{OH}$$

is proposed by these authors to occur, where $\text{VN}_x\text{O}_y||\text{OH}^-$ represents the electrochemical double layer formed by the hydroxy ions adsorbed on non-specific sites. A large increase in specific capacitance arises primarily due to successive oxidation by the hydroxyl species on the VN$_x$O$_y$ surface due to electron transfer across the double layer [81]. The CV curves change to an elliptical shape at high scan rates, indicating that some conductivity or diffusion limitation may appear for the oxynitride material in a three-electrode cell.

Furthermore, this behaviour can be also demonstrated in a CD test in Figure 4.4(b). The CD curves of tungsten oxynitride have a plateau at -0.98 V during
discharging, and arc-shaped curve can be observed at -0.57 during charging process. This Faradaic pseudocapacitive behaviour can provide more capacitance than electrochemical double layer alone to obtain high specific volumetric capacitance of 103 F/cm³ at a current density 0.05 A/cm³. The volumetric capacitance is calculated by the formula below:

\[ C = \Delta t \frac{I}{\Delta V \cdot v} \]

which \( \Delta t \) is the time of charging or discharging, \( I \) is the current, \( \Delta V \) is the potential window and \( v \) is the volume of the working electrode in a three-electrode system or the combined volume of two electrodes in a symmetric system.

However, the remaining capacitance is only 43 F/cm³ at a high current density (1 A/cm³) in Figure 4.4(d). The EIS shows that the charge transfer resistance of vanadium oxynitride in KOH solution is around 10 Ω. This relatively poor rate capability result is only prominent in the three-electrode system (and not in a symmetric cell), which is shown in the next section. The electrical resistivity can also be correlated with ohmic drop in charging and discharging processes (Figure 4.4c).
Figure 4.5 Electrochemical properties of tungsten oxynitride in 3M KOH in a three-electrode cell. (a, b) cyclic voltammetry tests at scan rates between 2 and 500 mV/s, (c) galvanostatic charging/discharging tests for the current densities between 0.05 and 1 A/cm², (c) electrochemical impedance spectroscopy test, and (d) plot of specific volumetric discharge capacitance vs current density.

The electrochemical performance of a tungsten oxynitride electrode is shown in Figure 4.5, which includes CV results at low scan rates (Figure 4.5a) and high scan
rates (Figure 4.5b), CD results at various current densities between 0.05 and 1 A/cm³, and the dependency of volumetric capacitance during discharging on the current density. It can be seen from the CV curves (recorded at a slow scan rate) that their shape is close to an ideal rectangular shape and is close to mirror-symmetric with respect to x-axis. One possible explanation is that tungsten oxynitride has standard electrochemical double layer capacitive behaviour during charging and discharging.

However, recent reports also indicate that the storage mechanism of tungsten oxynitride has not only electrochemical double layer capacitive behaviour but also involves pseudocapacitive process [85, 86, 123]. It is possible that that oxidised surface layers on the surface of tungsten oxynitride created after the synthesis contribute redox reactions during charging and discharging in KOH solution. Ideal-type triangular curves may be also visible galvanostatic charge/discharge results in Figure 4.5(c). Figure 4.5(d) presents the dependence of the volumetric capacitance on the current density. It can be seen that the capacitance first increases from 19.5 to 21 F/g (with the increase in current density from 0.05 to 0.2 A/cm³) and subsequently decreases to lower values. The initial behaviour of the electrode can be explained by the activation of the material.

### 4.3.3 Electrochemical properties of vanadium oxynitride and tungsten nitride in symmetric cells
Figure 4.6 Electrochemical properties of vanadium oxynitride in 3M KOH in a symmetric cell. (a and b) cyclic voltammetry test for the scan rates varied between 2 mV/s to 2 V/s, (c and d) galvanostatic charging/discharging test for the current densities varied from 0.05 and 10 A/cm$^3$, (e) electrochemical impedance spectroscopy test, and (f) the dependence of the specific volumetric discharge capacitance on the current density.
In order to investigate the properties of vanadium oxynitride and tungsten oxynitride in full cell devices, these electrode materials are tested in symmetric systems. Two identical electrodes (with weights closely matching each other) are assembled in a sandwich configuration with a separator in between in each case. The potential window of vanadium oxynitride in the CV test is from 0 to 1.2 V at various scan rates (between 2 mV/s and 2 V/s). It can be seen in Figure 4.6(a, b) that the shape of CV curves deviates somewhat from the rectangular shape and contains some redox reaction peaks at scan rates below 500 mV/s. The shape of the CV curves changes to the elliptical shape at very high scan rates of 1 and 2 V/s. The oxidation and reduction redox peaks of vanadium oxynitride are visible at 0.4 V and 0.6 V during charging and discharging. The shapes of the CD curves (Figure 4.6c, d) are much closer to the triangle shape than those obtained in a three-electrode cell but deviate from the ideal shape, nevertheless. It can be concluded that vanadium oxynitride’s reaction mechanism includes both electrochemical double layer capacitance and pseudocapacitive behaviours in KOH electrolyte. The charge transfers resistance of vanadium oxynitride measured from the EIS test (Figure 4.6e) is lower than 2 Ω. The discharge volumetric capacitance calculated from galvanostatic charge/discharge is 14.6 F/cm³ at 0.05 A/cm³ and remains at the level of 6.8 F/cm³ at 10 A/cm³.

The tungsten oxynitride electrodes are also tested in a symmetric cell, and the results are shown in Figure 4.7. The practical potential widow of tungsten oxynitride
is between 0 to 0.8 V in the KOH electrolyte during charging and discharging. Figure 4.5(a, b) show the CV tests performed at various scan rates. The classic rectangular shapes of the CV curves are kept until the scan rate of 1 V/s. Accordingly, the shapes of the CD curves are also symmetric and triangular. The capacitance of tungsten oxynitride mainly contribute by mesoporous structure on the surface of materials where electrochemical adsorption and desorption takes place during charging and discharging. The charge-transfer resistance of tungsten oxynitride in KOH is around 2 Ω and is approximately the same as that of the vanadium oxynitride cell. It can be concluded that these two oxynitrides are very conductive in the full cell devices.

The charge transfer resistance is very low for both materials in the symmetric cells when compared to that recorded in three-electrode cells. The values obtained from the three-electrode cells are around 10 Ohm and the values measured from the symmetric cells are not more than 2 Ohm. This discrepancy may originate from the relatively large distance between counter electrodes (Pt wires) and working electrodes in three-electrode systems. This distance is usually minimised in three-electrode cells but cannot be fully optimised in practical cells in certain situations. In contrast, the distance between two working electrodes is minimal (with only thin separator in between) in symmetric cells, and the transport limitations do not affect electrodes to the same extent.
Figure 4.7 Electrochemical properties of tungsten oxynitride in 3M KOH in a symmetric cell. (a, b) cyclic voltammetry tests for the scan rates varied between 2mV/s and 5 V/s, (c) galvanostatic charging/discharging tests for the current densities between 0.05 and 1 A/cm$^3$, (d) electrochemical impedance spectroscopy test, and (e) specific volumetric discharge capacitance vs current density.
Figure 4.8 The cycling stabilities of symmetric capacitors with (a) vanadium oxynitride and (b) tungsten oxynitride at a current density of 0.5 A/cm$^3$ in 3M KOH aqueous electrolyte.

It can be seen from Figure 4.8 that vanadium oxynitride and tungsten oxynitride symmetric cells are capable of retaining reasonably stable capacitances after 1000 cycles of charging and discharging at 0.5 A/cm$^3$. Tungsten oxynitride keeps around 99% capacitance after 1000 cycles. The stability of vanadium
oxynitride is somewhat inferior and the cell can maintain only 85% of its capacitance after 1000 cycles. This may originate from more prominent redox reactions in this material at the interface with KOH, which leads to a faster degradation of the electrodes during charging and discharging. The volumetric energy densities for the two full cells are also calculated and found to be 2.2 and 0.7 Wh/L, respectively for vanadium and tungsten oxynitride cells, respectively.

4.4 Conclusions

The nanoporous vanadium and tungsten oxynitrides are prepared by temperature-programmed NH₃ reduction method. The morphology of these materials are observed in SEM and electrochemical properties are measured through CV, GC and EIS methods in both three-electrode and symmetric cells. The two electrode materials operate in the 3M KOH electrolyte, and both electrochemical double layer capacitance and pseudocapacitive behaviour contribute to the charge storage. The maximal volumetric capacitances of vanadium and tungsten oxynitrides are 103 and 21 F/cm³, respectively. These electrode materials are very stable in KOH electrolyte and retain above 98% of their capacitance after 1000 charge-discharge cycles. The obtained information is useful for the development of power sources requiring compact footprint and volume minimisation.
Chapter 5: Activated carbon and graphite electrode materials for hybrid K-ion capacitors: electrochemical tests of individual electrodes and suggestions for designing the full cell capacitor

5.1 Introduction

As outlined in Chapter 1, two types of supercapacitors, symmetric and asymmetric (hybrid) systems, have been suggested. They may utilise aqueous or nonaqueous electrolytes. The energy density of classical symmetric supercapacitors with organic electrolytes is higher than that of cells with aqueous electrolytes due to a wider operational potential window; however, the energy density of current commercialised symmetric supercapacitors (Cap-XX, Maxwell) is still low [24]. The reason of this poor status is that most of conventional supercapacitors utilise two electric double layer electrodes (e.g., made of activated carbons), and this leads to low capacity and energy density. It has been proposed that a battery-type electrode may replace one of them to assemble an asymmetric supercapacitor with enhanced energy density. In particular, Amatucci’s group have developed the so called lithium-ion (hybrid) capacitor by using nanostructured Li$_4$Ti$_5$O$_{12}$ as the anode and a high surface area activated carbon as the cathode [124]. A high energy density has been achieved in this hybrid capacitor (58.5 Wh/kg).
Instead of lithium titanium oxide, other high capacity anode materials can be used; graphite, in particular can deliver a theoretical capacity of 372 mAh/g. In addition, graphite is also attractive to be used as an anode material in Li-ion hybrid capacitors due to its low redox potential (typical plateaus at 0.1-0.3 V vs Li/Li⁺) [125, 126]. The possibility of a quick removal of lithium from graphite (fast delithiation) has been demonstrated by Pandolfo et al. [127]. This performance suggests that the graphitic anode is able to contribute more power density for the full cell hybrid lithium-ion capacitors than other candidates. Graphite can also be pre-lithiated before its use in a full cell device. Since then, some companies have utilised this technology to produce commercial devices with lithiated graphite as the anode and an activated carbon as the cathode; Li-ion capacitors of this type are manufactured by JSR Micro, Inc. (Japan) and are distributed under the trade name ULTIMO [128].

Similar to its lithium counterpart, another hybrid capacitor can be built on K⁺ ions as well. It has been recently demonstrated that graphite as an anode material can work in a potassium ion organic electrolyte in a battery system [129]. The advantage of potassium ion-based systems is a possibility to prepare high voltage cells, possessing high energy densities. Based on this research, it is anticipated that potassium-ion hybrid capacitors with graphitic anodes can function in organic electrolytes. Cathodes based on activated carbons can be used, most likely, but has not been demonstrated as yet. Finally, it is predicted that the ionic migration rate of K⁺
ions is much higher than that of Li\(^+\) ions or Na\(^+\) ions. Organic electrolytes such as KPF\(_6\) in EC/DEC (1:1) can be utilised for K-ion devices. [130]. Therefore, K-ion capacitors are alternative candidate devices with energy storage performances superior to conventional supercapacitors. In order to investigate the electrochemical properties of K-ion capacitors, graphite and activated carbon are the promising candidates for the roles of electrode materials due to their anticipated battery-type and capacitive operation at low and high potentials vs K/K\(^+\) reference/counter electrode, respectively.

In this chapter, I prepare half-cell configurations to evaluate each electrode material separately for its prospective application in K-ion capacitors with high energy density. The electrode materials are initially characterised by SEM, Raman spectroscopy and nitrogen adsorption/desorption. Electrochemical properties of activated carbon and graphite are tested in coin cells utilising potassium foil as a reference/counter electrode. In the second part of the chapter, possible design of a full cell K-ion capacitor was discussed. In particular, the voltage profile of this new electrochemical cell is discussed, and recommendations about electrode pre-cycling and balancing in the full cell are given.

5.2 Experimental

5.2.1 Preparation of electrodes and coin cells

Activated carbon (YP-50F, Kuraray Chemical Co.) and graphite (Sigma Aldrich, <20 \(\mu\)m) were used as electrode materials. Activated carbon was mixed with
carbon black as a conductor and CMC powder as a binder with the weight ratio of 8: 1: 1. The mixture was ground homogeneously in a mortar for 30 min until metallic appearance was achieved. Next, de-ionised water was added to the mortar, and the resulting slurry was further ground. Finally, the slurry was coated on pieces of Al foil.

To prepare graphite-containing electrodes, the active material was mixed with carbon black as a conductor and PVDF powder as a binder with the weight ratio of 8: 1: 1. The dry mixture was initially ground dry in a mortar, and NMP solvent was subsequently added. Both types of electrodes were initially dried at room temperature for 2 h. They were eventually relocated into a vacuum oven and kept overnight under vacuum at 70°C to make sure the inside of electrodes dried completely. The electrochemical cells for both electrodes were assembled in the form of coin cells to test the electrochemical properties. Activated carbon or graphite as working electrodes and potassium metal foils as counter/reference electrodes were assembled into the half-cells with 0.75 M KPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 as an electrolyte in a glove box under the protection of argon gas.

5.2.2 Characterisation

SEM (Carl Zeiss Supra 55VP instrument) was used for the visualization of the morphology of materials and Raman spectroscopy (Renishaw inVia microspectrometer) was used for the evaluation of the quality of graphitic structure.
Nitrogen adsorption and desorption (Micromeritics Tristar system) was used to probe the porous structure of samples and BET method was applied for calculating the value of specific surface area. The electrochemical performances were tested on the Land battery system (Wuhan Land, China) for low current density experiments and Solartron Analytical 1470E electrochemical workstation for high current density experiments. The tests were divided into two groups. The first group of activated carbon and graphite cells were tested by galvanostatic charging and discharging at 50 mA/g and 25 mA/g, respectively, for hundreds of cycles. The second group of experiments included testing by galvanostatic charging and discharging at varied currents between 50 mA/g to 1 A/g and 25 mA/g to 1 A/g.

5.3 Results and discussion

5.3.1 Evaluation of morphology and structure in the graphite and activated carbon electrode materials
TY-50 activated carbon and commercial graphite were characterised by field emission scanning electron microscopy in order to investigate the morphology. The images are shown, respectively, in Figure 5.1 and Figure 5.2. The particles of activated carbon with the size range from 1 to 10 µm are observed in Figure 5.1(a). At the micro-scale, activated carbon particles with high conductivity can increase the migration of electrons inside and also provide developed porous structure for the migration of ions during an electrochemical process. Figure 5.1(b) depicts a single particle at a high magnification. Pores can be observed on the surface of this single particle. The pore size is less than 100nm, which means that the porous structure of
activated carbon is predominantly in the range of micropores (< 2nm) and mesopores (2 - 50nm). The porous structure assists ion adsorption and desorption from the electrolyte.

For the commercial graphite, blade-shaped particles with sizes of around 2 µm are seen in SEM images (Figure 5.2a). Each blade has a layered structure, which can be observed in Figure 5.2(b). The typical thickness of the visible graphitic stacks is between 200 and 400 nm. The ions are expected to intercalate from the side surfaces of graphitic platelets into the interlayer spacings. Therefore, the mechanisms
of charge storage in these two electrode materials are expected to be quite different. It is an expectation that activated carbon and graphite can be assembled into a full cell hybrid potassium-ion capacitor as the cathode and anode, and may operate via adsorption and intercalation mechanisms, respectively.

![Raman spectra of activated carbon and graphite](image)

Figure 5.3 Raman spectra of YP-50F activated carbon and commercial graphite.

Raman spectra of activated carbon and graphite are shown in Figure 5.3. The D-band of activated carbon and graphite is located at a Raman shift of 1343 cm⁻¹. Meanwhile, the Raman spectra display the G-band of activated carbon and graphite at 1590.2 cm⁻¹ and 1563.7 cm⁻¹ respectively. As it can be seen in this figure, a high intensity of G-band and a low intensity of D-band of graphite indicate that the commercial graphite has a high degree of ordering in the graphitic structure. This crystal structure is associated with good electrical conductivity and the ability to
insert ions into the spaces between the layers to form intercalation compounds. In the case of activated carbon, the G-band is shifted to a higher frequency of 1590 cm\(^{-1}\), which indicates that YP-50F activated carbon has a disordered structure. It can be noted that D-band of the activated carbon is somewhat higher than G-band. In addition, full widths at half maxima (FWHMs) of both D and G bands are larger for the activated carbon than those of the commercial graphite. In order to enhance the electrochemical property of disordered carbon, the porous structure is another important reference and is discussed next.

![Nitrogen adsorption/desorption isotherms of YP-50F activated carbon and commercial graphite.](image)

*Figure 5.4 Nitrogen adsorption/desorption isotherms of YP-50F activated carbon and commercial graphite.*
Table 5.1 BET surface areas and parameters of porous structure for YP-50F activated carbon and commercial graphite.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_1 ) (cm(^3)/g)</th>
<th>( V_m ) (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>1282</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>Graphite</td>
<td>10</td>
<td>0.024</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure 5.5 Pore size distribution of activated carbon via BJH method.

The nitrogen adsorption/desorption isotherms of activated carbon and graphite are shown in Figure 5.4 and the parameters of porous structure are shown in Table 5.1. The graph of the activated carbon belongs to Type I of physisorption isotherms, which are characteristic of microporous solids having relatively small external surface area [35]. The nitrogen adsorption/desorption isotherm of graphite can be considered as Type II isotherm, which represents unrestricted monolayer-
multilayer adsorption or desorption at a low surface area. As shown in Table 5.1, the surface areas of activated carbon and graphite are 1282 and 10 m²/g. The pore size of activated carbon is typically located in the micropore range, which correlates with pore size distribution in Figure 5.5.

5.3.2 Electrochemical properties of activated carbon and graphite in potassium half cells and suggestions for designing a full cell device

5.3.2.1 Half-cell performance of the activated carbon and graphite electrodes

![Graphs showing electrochemical properties](image)

*Figure 5.6 Electrochemical properties of activated carbon in potassium half-cells: (a) the capacity and cyclic stability at a 50mA/g current density; (b) the capacity of activated carbon at a multi-current density 50 mA/g and 100 mA/g; (c) charge and discharge curves at 50 mA/g; (d) charge and discharge curves at 200mA/g.*
In order to investigate the electrochemical properties, the galvanostatic charge-discharge of activated carbon and graphite was tested in half-cells. The electrochemical properties of activated carbon are shown in Figure 5.6. It can be seen that activated carbon can be working in the organic electrolyte of KPF$_6$ (in EC:DEC) with charge-discharge curves of a triangular shape. Hence, the activated carbon has the double layer capacitive behaviour in a potassium half-cell during charging and discharging. This characteristic can appear through ion adsorption of either K$^+$ or PF$_6^-$ on the surface of pores in the cathode. The highest useful potential was considered to be 4 V vs K/K$^+$, and the potential window of about 2 V was measured for the electrode, which means activated carbon has a broad useful potential range in the KPF$_6$ electrolyte. The highest charge capacity of this material is 56 mAh/g at a 50 mA/g current density and 40 mAh/g discharge capacity is observed. A capacity of 27 mAh/g remains at a current density of 100 mA/g.
Figure 5.7 Electrochemical properties of graphite in potassium half-cells: (a) the capacity and cyclic stability of graphite at a 25 mA/g current density; (b) the specific capacity of graphite at a multi-current density from 25 mA/g to 1 A/g; (c) charge and discharge curves at 25 mA/g; (d) charge and discharge curves at 200 mA/g.

Figure 5.7 shows the electrochemical performance of graphite in potassium half-cells. As it can be seen in Figure 5.7(c) and (d), the galvanostatic charge and discharge curves are not triangular in shape. Instead, there are charge and discharge plateaus at 0.2-0.3 V vs K/K⁺, indicating intercalation behavior, similar to that for graphite in lithium cells. Figure 5.7(a) shows that the charge capacity of graphite in a potassium cell can be up to about 300 mAh/g, and it remains 127 mAh/g after 100 cycles. The observed specific capacity is much higher than that of graphitic materials in aqueous supercapacitor systems [131, 132]. The power density of graphite is not expected to be particularly high, from the results of the multi-current test shown in
Figure 5.7 (b). The capacity of graphite electrode drops to 9.3 mAh/g at 1A/g current density. This property needs to be improved in the future work. There is, however, a report that quick depotassiation can be achieved after the potassiation of graphite [130], and this may be a possible way to improve rate performance of graphite electrodes.

5.3.2.2 Suggestions for the design of a full cell K-ion capacitor

Based on the results for individual electrodes outlined in the previous section, I discuss a possible design of a full cell potassium-ion capacitor in this section. For a full cell hybrid capacitor, two different electrodes are used in this device. One of them (usually cathode) should be an EDLC electrode such as an activated carbon discussed in this chapter. Another electrode (usually anode) should be a battery-type electrode. Graphite can be such an electrode as shown in Figure 5.7. Overall, I suggest that a hybrid potassium-ion capacitor can utilise YP-50F activated carbon as the cathode and commercial graphite as the anode. Before this type of device is assembled practically though, it needs to be understood how a capacitor-type voltage profile is achieved for the cell and how to pre-cycle (or pre-potassiate) and balance the electrodes in terms of their weights. I discuss these aspects further below.

As it is shown in Figure 5.6(c), the potential range of activated carbon is 2-4.2 V vs K/K⁺ in a half-cell, and its charge-discharge profile is triangular. In contrast, the charge-discharge profiles of graphite show plateaus at about 0.2-0.4 V vs K/K⁺. For the simplicity of the conceptual discussion, let us assume that the charge and
discharge of graphite happen at a fixed voltage which is equivalent to 0.3 V vs K/K\(^+\) in graphite half-cell, and the charge-discharge profiles of the capacitive electrode are perfectly triangular (Figure 5.8a). In the full cell, the voltage range of the whole device is the difference between potentials of the cathode and anode, following the equation:

\[ V_{\text{full1}} = V_1 - V_0, \quad V_{\text{full2}} = V_2 - V_0, \]

where \( V_{\text{full1}} \) is lowest practical voltage in the full-cell, \( V_{\text{full2}} \) is the top of the voltage range in full-cell, \( V_1 \) is the lowest potential of activated carbon \(^+\) in half-cell, \( V_2 \) is the highest voltage of activated carbon in half-cell, and \( V_0 \) is the potential of the plateau of the battery electrode. Thus, according to the equation and the charge-discharge profiles of individual electrodes, the lowest voltage of this hypothetical device should be 1.7V (with slight possible deviations, considering the real charge-discharge profiles of the electrodes) and the anticipated highest voltage for the device is 3.9V, as shown schematically in Figure 5.8(b).
When tested in half-cells, both activated carbon and graphite electrodes have the same counter/reference electrode, a potassium metal foil. This counter electrode is an infinite source of $\text{K}^+$ ions and allows the opposite electrode in a half-cell to be either charged or discharged. The situation for the full cell is different, as both the anode (graphite) and the cathode (activated carbon) do not contain potassium by default. That may lead to an inferior energy density for the full cell because the device may need to be charged initially to potassiate the graphitic anode but only a part of the charge profile of the activated carbon will be utilised (the initial starting potential is higher than the low boundary of the potential window in this electrode), and therefore the cathode in such a cell needs to be oversized to compensate for this. As a result, pre-potassiation of the anode is beneficial. This can be achieved through the use of an auxiliary (third) metal electrode (as it is done in commercially available lithium-ion capacitors) or via electrochemical pre-cycling of the anode. An optional pre-cycling of the cathode (activated carbon) can be done as well.

In the scenario in which both electrodes are initially pre-cycled, I recommend pre-cycling for three cycles to eliminate the inefficiencies of the initial cycles and also to tune the electrodes to useful potentials required for the operation of the full cell. In particular, graphite as an anode should be pre-cycled and discharged to 0.35
V vs K/K\(^+\) potential in a half-cell. This will condition the graphitic electrode to be set at the onset of its plateau (as shown in Figure 5.9a). Activated carbon as a cathode should be pre-cycled three times and discharged to 2.0 V vs K/K\(^+\) potential in a half-cell. This sets the electrode at a potential corresponding to the bottom of its triangular profile (Figure 5.9b). Subsequently, both half-cells need to be disassembled, and graphite and activated carbon electrodes need to be extracted from each cell. The pre-cycled anode and cathode are then reassembled in a new cell to compose a full cell device. The assembled cell is expected to be in the discharged state initially and will need to be charged during the initial operation.

Alternatively, only the anode needs to be pre-cycled. In this scenario, the initial potential of the cathode is at a level of initial potential in a half-cell, that is, typically within 0.28-0.32 V range vs K/K\(^+\) (Figure 5.9c). In order to utilise the capacities of both cathode and anode fully, the graphite needs to be pre-cycled to a more potassiated state in this case, at around 0.23-0.25 V vs K/K\(^+\) in a half cell (Figure 5.9d). If this is done and assuming that the capacities of the two electrodes are matched, the specific energy density will be maximized for a cell in which the activated carbon cathode not pre-cycled before the assembly.
Figure 5.9 Schematic representation of pre-cycling routines for the graphite and activated carbon electrodes: (a, b) in a scenario in which both cathode and anode are pre-cycled; (c, d) in a scenario in which only anode is pre-cycled. The charge-discharge curves and termination points for the graphite electrodes are shown in (a) and (d), and those for the activated carbon are shown in (b) and (c). Note that the cathode in (c) is not pre-cycled as used in the full cell directly as is.

Importantly, the anode and cathode in the potassium-ion cell must be balanced in terms of the weights of active materials. This is usually achieved by matching the capacities of the two electrodes. For this reason, the weight of activated materials of the two electrodes is, for example, similar in conventional symmetric supercapacitors to make sure that the capacity of each electrode is the same. In contrary, the specific capacities of an anode and a cathode are quite different in a hybrid capacitor system,
and using electrodes with different weights is inevitable to avoid a situation when the capacity of one of the electrodes cannot be used fully. According to my measurements, the highest specific capacity of a graphite electrode is 684.5 mAh/g. Meanwhile, the highest specific capacity of an activated carbon electrode is 58.2 mAh/g. As it follows, the gravimetric specific capacity of graphite is approximately 11.8 times higher than that of activated carbon. Therefore, the quantity (weight) of the anode should be generally 11.8 times higher than that of the cathode. For example, if the weight of graphite as an anode is 10 mg, the weight of activated carbon as a cathode is recommended to be 118 mg. In this scenario, all material in both anode and cathode can be fully used during charging or discharging. The gravimetric capacity of the whole device is able to reach the maximum value. As a consequence, the gravimetric energy density will be at the maximum value as well.

5.4 Conclusions

In this chapter, activated carbon (YP-50F) and commercial graphite materials are considered as cathode and anode materials for potassium-ion hybrid capacitors. The two electrode materials were characterised by SEM, Raman, and N\textsubscript{2} adsorption/desorption. These methods are used to investigate the morphology, perfection of the graphitic structure and textural characteristics such as surface area and pore size distribution. A high surface area of activated carbon contributes to its EDLC capacity in K-ion capacitors. The layered structure of graphite is able to
intercalate potassium ions. In terms of their electrochemical performance, activated carbon and graphite demonstrate capacitive and battery-type behaviours, respectively, in half-cells with KPF₆ EC/DEC (1:1 by volume) electrolyte.

Finally, suggestions for constructing a full cell device of an activated carbon/graphite hybrid capacitor are given. A device is expected to operate within an expected voltage range of 1.7 – 3.9 V with a capacitor-type charge-discharge profile. It is recommended for practical purposes that the anode (graphitic material) is pre-potassiated. At a demonstration stage, this can be achieved by pre-cycling graphitic electrodes in half-cells. The pre-cycling of activated carbon is optional, but affects the degree of potassiation required in the graphitic electrodes. The importance of electrode balancing in terms of their weights in a full cell device is also highlighted.
Chapter 6: Summary and future work

Electrode materials for electrochemical supercapacitors with electrolytes containing potassium (K\(^+\)) ions were investigated in this thesis. In particular, I studied five different types of nanostructured electrode materials, including titanium dioxide nanotubes, nanoporous vanadium and tungsten oxynitrides, activated carbon and graphite. All these electrode materials are able to work in the electrolyte systems containing potassium ions. Among various potassium-containing electrolytes, neutral aqueous electrolyte potassium chloride (KCl) solution, alkaline aqueous potassium hydroxide (KOH) solution and non-aqueous potassium hexafluorophosphate (KPF\(_6\)) in EC/DEC (1:1) were used. It was demonstrated in this thesis that various materials studied had promising applications in three different areas of the electrochemical energy storage field. For example, a thin film of TiO\(_2\) nanotubes has good biocompatibility and is able to work in a simulated body fluid, K-rich phosphate-buffered saline (PBS) solution, with satisfactory behaviour. Nanoporous V(N,O) and W(N,O) oxynitrides can potentially have high volumetric capacitances and can be applied in power sources with reduced footprint and size. High energy density hybrid potassium-ion capacitors were proposed and can be assembled using activated carbon as a cathode and graphite as an anode. All these aspects of supercapacitors were studied in detail and were presented in this thesis.
Films of titanium dioxide nanotubes, the first electrode material, were grown on a titanium metal plate as a thin film via anodization method. The films were treated at three different annealing temperatures - 600, 650 and 700 °C. The X-ray diffraction experiments revealed that phase changes occurred in the films, and different contents of anatase and rutile phases were detected in these samples. The morphologies of all samples were identified to be quasi-aligned nanotubes by scanning electron microscopy. The initial electrochemical assessment of TiO$_2$ in KCl solution revealed that films had an ideal rectangular shape of the CV curves and a triangular shape in the charge-discharge test. The specific capacitance of this material in KCl solution can be up to 1700 µF/cm$^2$ at a low current density and remains at a level of 1100 µF/cm$^2$ at a high current density. Anodized titanium dioxide nanotubes have high biocompatibility, that is, can be potentially compatible with the environment of a body. Phosphate-buffered saline (PBS, pH 7.4) was used to simulate the human body fluid in supercapacitors and is another example of a potassium-rich electrolyte. The electrochemical results showed that specific discharge capacity of this materials could be as high as 2817 µF/cm$^2$, and a stable capacity of 640 µF/cm$^2$ was demonstrated for 1000 cycles. These novel results demonstrate that TiO$_2$ is a promising biocompatible electrode material capable of working in potassium-containing electrolytes.
Vanadium and tungsten oxynitrides were produced by the temperature-programmed reduction of the commercially available oxide powders in ammonia (up to a stationary temperature of 700°C). Such a preparation process leads to nanoporous structures. The phases of V$_{0.7}$(N,O) and W$_{0.6}$(N,O) were identified via XRD and WDS. The nanopores were observed on both materials from SEM images. Vanadium oxynitride had a 1.2 V operational potential window, with contribution from both EDLC and pseudocapacitive mechanisms to provide a high volumetric capacity of 103 F/cm$^3$ at a 0.05 A/g current density. The tungsten oxynitride electrode material had an ideal shape of its electrochemical curves. This may be an indication that the EDLC process is dominant in an aqueous KOH electrolyte for this electrode. A limited volumetric capacitance of 21 F/cm$^3$ was measured at a low current density, and the operational potential window was only 0.8 V. The thicknesses of vanadium and tungsten oxynitride electrodes were measured for calculating the volumetric capacitances, as well energy and power densities for symmetric supercapacitor systems assembled with these electrodes in this thesis. The full symmetric devices with electrodes of vanadium and tungsten oxynitrides were assembled to obtain 2.2 and 0.7 Wh/L energy densities, respectively. Both of them had good stability after 1000 cycles of charge-discharge.

Subsequently, activated carbon and graphite were explored as potential cathode and anode materials for potassium-ion capacitors. The nanoporous structure
of activated carbon and pronounced layered structure of graphite were shown by SEM images. The nitrogen adsorption/desorption was utilised for activated carbon to measure its specific surface area (BET method) and pore size distribution. The extent of graphitization of each sample was examined via Raman spectroscopy. Electrochemical properties of these materials were tested individually in half-cells. Activated carbon showed an ideal EDLC behaviour in the half-cell with non-aqueous electrolyte (KPF₆ in EC/DMC), and a capacity of 56 mAh/g was recorded. The cyclic stability over 1000 cycles was promising. The electrochemical signatures of graphite in half-cells were battery-type, with prominent plateaus. The plateaus in the galvanostatic charge-discharge curves indicate that ion intercalation/deintercalation happens in this electrode material. The reversible capacity of graphite was up to slightly below 300 mAh/g at a 50 mA/g current density. However, the rate capability of this material needs improvement in order to realise high-power devices. Suggestion for the design of a full cell potassium-ion capacitor were given as well. In particular, electrode materials need to be matched in terms of their capacities, and, accordingly, the weights of the two electrodes need to be balanced. The anode (graphite) may benefit from pre-potassiation, and the depth of pre-potassiation may depends on if the cathode material (activated carbon) is pre-cycled or used as-is. It was anticipated that the potassium-ion capacitor could be a high voltage electrochemical cell (~3.9 V).
The results in this thesis demonstrate that there are differences and similarities in the behaviour of various electrodes in supercapacitor cells with potassium-containing electrolytes. For example, it is widely known that there are two types of electrochemical storage mechanisms in conventional supercapacitors, electrochemical double layer capacitive (EDLC) process and Faradaic pseudocapacitive mechanism. In some cases, one of this mechanisms is dominant, while both charge storage mechanisms may co-exist for some electrode materials. For example, it appears that titanium dioxide functions in the aqueous KCl electrolyte via a classical EDLC process. Indeed, it can be seen in Chapter 3 that titanium dioxide nanotube has an ideal rectangular shape of cyclic voltammetry curves. EDLC process appears dominant not only in titanium dioxide nanotubes but also in porous tungsten oxynitride and activated carbon. In contrast, EDLC process occurs simultaneously with the Faradaic pseudocapacitive mechanism in vanadium oxynitride electrodes operating in KOH solution, as it was shown in Chapter 4. Finally, it is worthwhile to note that battery-type materials can also be combined together with capacitive materials in high voltage capacitor cells, and one of such materials, graphite, was discussed in Chapter 5.

Furthermore, it is anticipated that there may be specific advantages of using potassium-containing electrolytes for supercapacitors or hybrid capacitors. For example, hybrid capacitors utilising potassium are expected to have a higher
operating voltage than their sodium counterparts. It has been also speculated that K+ has a higher migration rate in some electrolytes then that of Li⁺ or Na⁺. TiO₂ films were found to maintain 73% of their capacitance at a high current density. Vanadium oxynitride may achieve a wide operating potential window of around 1.2 V in aqueous potassium hydroxide electrolyte to provide a higher energy density in full cell devices. It is also anticipated that K-ion capacitors with graphite and activated carbon electrodes may operate in the voltage range between 1.7 and 3.9 V, similar to that of Li-ion hybrid capacitors. Importantly, the electrode materials considered in this thesis may be utilised in potassium-based electrolytes in a number of application-specific types of supercapacitors including biocompatible supercapacitors, supercapacitors with minimised footprint and new high voltage hybrid capacitors.

It is my expectation that future work by other researchers will build on the results from this thesis. The following main directions for the future work can be recommended. TiO₂ nanotube thin films should be treated in the air at different temperature in the future work which can be compared with the treatment in the Ar. TiO₂ nanotube thin films should be used to assemble the full cell devices with PBS or other electrolytes imitating body fluids. Such devices could further verify the potential of titanium dioxide electrodes for the application in implantable and wearable supercapacitors. The assessment of the volumetric parameters of vanadium and tungsten oxynitride electrode was performed only in symmetric electrochemical
cells in this thesis. It is recommended that these electrodes are also evaluated in asymmetric supercapacitor from the point of view of their volumetric performance. Finally, suggestions for the design of a hybrid potassium-ion capacitor with activated carbon and graphite electrodes were given. Further experiments are necessary to be conducted in order to demonstrate a functional prototype of this high voltage device.
References


[40] Wang, H & Yoshio, M 2006, 'Graphite, a suitable positive electrode material for high-energy electrochemical capacitors', Electrochemistry Communications, vol. 8, no. 9, pp. 1481-1486.


transfer of electrons', *Journal of the American Chemical Society*, vol. 130, no. 40, pp. 13364-13372.


and anatase TiO₂ for lithium insertion using anodic TiO₂ nanotube arrays', *Nanotechnology*, vol. 20, no. 22, p. 225701.


[81] Choi, D, Blomgren, GE & Kumta, PN 2006, 'Fast and reversible surface redox reaction in nanocrystalline vanadium nitride supercapacitors', *Advanced Materials*, vol. 18, no. 9, pp. 1178-1182.


110


[130] Komaba, S, Hasegawa, T, Dahbi, M & Kubota, K 2015, 'Potassium intercalation into graphite to realize high-voltage/high-power potassium-ion batteries and potassium-ion capacitors', *Electrochemistry Communications*, vol. 60, pp. 172-175.
