

**POLYURETHANE BINDER FOR MXENE
ELECTRODE FABRICATION OF HYBRID
SUPERCAPACITOR**

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**SCHOOL OF MATERIALS AND MINERALS
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UNIVERSITI SAINS MALAYSIA
2022**

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**POLYURETHANE BINDER FOR MXENE ELECTRODE FABRICATION OF
HYBRID SUPERCAPACITOR**

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Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)


Universiti Sains Malaysia

August 2022

DECLARATION

I hereby declare that I have conducted, completed the research and written the dissertation entitled “Polyurethane Binder for Mxene Electrode Fabrication of Hybrid Supercapacitor Studies”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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ACKNOWLEDGEMENT

First and foremost, I would want to convey my heartfelt gratitude and appreciation to Assoc. Prof. Dr. Ahmad Azmin Mohamad, my final year project supervisor, for providing me with crucial advice during this research. His immense knowledge, commitment, patience, and enthusiasm have greatly inspired and aided me in completing this thesis.

Furthermore, I am grateful to Ms Nor Azmira Salleh for her guidance and dedicated participation at every stage of this work, particularly in guiding me to properly handle the experimental equipment and supplies.

In addition, I would like to thank all of the technicians and staffs at the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, particularly Encik Mohd Azam Bin Rejab, Encik Abd Rashid Bin Selamat, Encik Muhammad Khairi Bin Khalid, Encik Mohamad Zaini Bin Saari, and Puan Haslina Binti Zulkifli, for their assistance and cooperation in completing my final.

Finally, I'd like to use this opportunity to express my heartfelt gratitude to my family and friends for their unwavering support, inexhaustible motivation, and constant encouragement during this effort. This feat would not have been accomplished without their understanding and cooperation.

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LIST OF ABBREVIATIONS

PU	Polyurethane
GCD	Galvanostatic charge-discharge
CE	Counter electrode
C_s	Specific capacitance
CV	Cyclic voltammetry
SEM	Scanning Electron Microscopy
RE	Reference Electrode
SCs	Supercapacitors
WE	Working Electrode
XRD	X-ray Diffraction

LIST OF SYMBOLS

%	Percentage
°	Degree
A g ⁻¹	Ampere per gram
mV s ⁻¹	Millivolt per second
F g ⁻¹	Farad per gram
s	Seconds
A	Ampere
cm	Centimeter
g	Gram
V	Volt

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PENGIKAT POLIURETANA UNTUK KAJIAN FABRIKASI ELEKTROD MXENE SUPERCAPACITOR HIBRID

ABSTRAK

Pengikat poliuretana (PU) dicampur dengan peratus berat badan yang berbeza (wt%) dengan titanium karbida (TiC) dan karbon aktif (AC) menggunakan N-metil-2pyrrolidone (NMP) sebagai pelarut dalam pembuatan elektrod pemuat lampau TiC-PU. Larutan TiC-PU 2, 4, 6, 8 dan 10 wt% disediakan. Pertama, PU dilarutkan selama 10 minit di dalam 5 ml NMP, kemudian TiC dan AC ditambah dan dikacau selama 2 jam dalam suhu bilik. Seterusnya, busa nikel (Ni) dicelupkan dalam larutan pada keluasan $1 \times 1 \text{ cm}^2$ dan dikeringkan selama 3 jam pada suhu bilik sebelum dikering di dalam oven pada suhu 80°C semalaman dan kemudian proses pencelupan diulang, menjadikan elektrod TiC-PU dua kali dicelup-kering. Morfologi menunjukkan bahawa TiC-PU 10 wt% mempunyai taburan permukaan TiC yang baik pada busa Ni dan lebih seragam berbanding dengan komposisi TiC-PU yang lain. Juga, XRD plot menunjukkan TiC-PU 10 wt% mempunyai plot Ni dengan intensiti terendah menunjukkan bahawa pengikat PU membentuk ikatan fizikal dan sifat penyebaran yang baik. Begitu juga plot voltametri kitaran (CV), TiC-PU 10 wt% menunjukkan tindak balas redoks yang baik dan mempamerkan kekuatan spesifik, yang tinggi iaitu 0.00124 F g^{-1} pada kadar imbasan 10 mV S^{-1} . Urutan kapasitansi khusus oleh pengikat TiC-PU adalah $10 \text{ wt\%} > 8 \text{ wt\%} > 6 \text{ wt\%} > 4 \text{ wt\%} > 2 \text{ wt\%}$. Untuk pelepasan caj galvanostatik (GCD), urutan kapasitansi tertentu oleh pengikat TiC-PU dari graf GCD adalah $10 \text{ wt\%} > 8 \text{ wt\%} > 6 \text{ wt\%} > 4 \text{ wt\%} > 2 \text{ wt\%}$ dan TiC-PU 10 wt% menunjukkan kekuatan spesifik tertinggi, iaitu 81.9076 F g^{-1} pada ketumpatan semasa 1.4 A g^{-1} . Ini membuktikan bahawa TiC-PU 10 wt% sebagai bahan elektrod yang baik untuk aplikasi supercapacitor yang bagus berbanding peratus berat TiC-PU yang lain.

POLYURETHANE BINDER FOR MXENE ELECTRODE FABRICATION OF HYBRID SUPERCAPACITOR STUDIES

ABSTRACT

Polyurethane (PU) binder was combined with titanium carbide (TiC) and activated carbon utilising N-methyl-2pyrrolidone (NMP) as a solvent to generate TiC-PU based supercapacitor electrode (SC). The slurry with different wt% of which are TiC-PU 2 wt%, 4 wt%, 6 wt%, 8 wt% and 10 wt%. After stirring PU for 10 minutes in 5ml NMP, TiC and AC were added and mixed for 2 hours at RT. After that, the slurry was dipped on Nickel (Ni) foam in 1 x 1 cm² and dried for 3 hours at RT before oven-drying at 80°C overnight this step was repeated on second day, making the TiC-PU electrode twice dipped-dried. The morphology shows that TiC-PU 10 wt% has a good TiC surface distribution on Ni foam and more uniform on Ni foam compared to the other composition of TiC-PU. Also, XRD plot shows that Ni peak by TiC-PU 10 wt% has the lowest intensity which proved that PU binder formed a great physical bond and spread-ability. Same goes to electrochemical characteristic shows that, TiC-PU 10 wt% displays a good redox behaviour and exhibited high specific capacitance for CV which is 0.00124 F g⁻¹ at scan rates of 10 mV s⁻¹. The specific capacitance by TiC-PU binders was 10 wt % > 8 wt % > 6 wt % > 4 wt % > 2 wt %. The greater amount of PU binder reduces the TiC active site and, as a result, the specific capacitance. The sequence of specific capacitance by TiC-PU binders from GCD curves was 10 wt % > 8 wt % > 6 wt % > 4 wt % > 2 wt %, with TiC-PU 10 wt % showing the maximum specific capacitance of 81.9076 F g⁻¹ at current density of 1.4 A g⁻¹. This revealed that the TiC-PU 10 wt% appeared to be a promising electrode material for supercapacitor applications compared to the other wt% of TiC-PU electrode.

CHAPTER 1

INTRODUCTION

1.1 Background

One type of energy storage system is known as a supercapacitors (SCs), which is also known as an electrochemical capacitor and an ultracapacitor. SCs are capable of storing and delivering energy at relatively high rates (above and beyond what is possible with batteries) due to the fact that the mechanism of energy storage is a simple charge separation at the electrochemical interface between the electrode and the electrolyte. When compared to dielectric capacitors, the energy density of SCs is significantly larger. This difference can be measured in orders of magnitude. SCs, on the other hand, have the potential to compensate for the shortcomings of traditional power sources such as batteries and fuel cells due to their long cycle life, and also rapid charging and discharging at high power densities. (Horn, MacLeod, Liu, Webb, & Motta, 2019; Y. Wang et al., 2009).

There are many advantages to using supercapacitors over other energy storage devices, including a longer lifespan, higher energy output per unit of weight and packing flexibility, a wider operating temperature range (-40° C to 70° C), and reduced maintenance (Das et al., 2022; Y. Wang et al., 2021). SCs encompass a combination of active and passive components (Loganathan et al., 2022). A supercapacitor is made up of a positive electrode, a negative electrode, electrolytes, an electrically non-conductive separator to prevent shorting between the two electrodes, and a pair of current collectors that connect the electrodes to the external circuit, as shown in Figure 1.2 (J. Chen & Lee, 2021).

The operation of a supercapacitor is predicated on the storage of energy as well as the transfer of ions from the electrolyte to the electrodes' surface areas (Das et al.,

2022). On the basis of the process by which they store energy, supercapacitors can be broken down into three distinct classes: Electrochemical double-layer capacitors, pseudocapacitors, and hybrid supercapacitors (Iro, Subramani, & Dash, 2016).

SCs are classified into three (3) types based on their energy storage technique. The first is an electrical double layer capacitor (EDLC), which achieves capacitance by accumulating pure electrostatic charge on the electrode electrolyte interface. This group is heavily reliant on the electrode surface area that is available to electrolyte ions. The second type is the pseudocapacitor, in which a quick and reversible faradic process occurs due to electroactive species (Sarno, 2020; Sudhakar & Krishnappa, 2019). The third category is hybrids, which combine the features of EDLC and Pseudocapacitors. The selection of electrode material is critical in supercapacitors since it determines the electrical properties (Berrueta, Ursúa, San Martín, Eftekhari, & Sanchis, 2019). Because double layer charge storage is a surface process, the surface quality of the electrode material has a large influence on the cell's capacitance (Iro et al., 2016).

The hybrid supercapacitor was the subject of this paper. In comparison to traditional electric double layer capacitors (EDLC) and pseudocapacitors, the hybrid supercapacitor has a larger specific capacitance (K. D. Verma, Sinha, Banerjee, & Kar, 2020). In general, the asymmetric behaviour of hybrid supercapacitors, which are a combination of EDLC and pseudocapacitor, functions as a capacitance enhancer (Maity, Goswami, Verma, Sahoo, & Nayak, 2020). A SCs is made up of two electrodes, an electrolyte, and a separator that electrically isolates the two electrodes (Rafidi et al., 2022).

Electrodes, electrolytes, and separators are the three main components of supercapacitors. The most significant component of a supercapacitor is the electrode

material. The electrochemical properties determined by a combination of electrode and electrolyte materials can be used to evaluate the performance of SCs (Raza et al., 2018). The materials used in supercapacitors' electrodes are an important aspect in determining their energy storage capability. Electrodes for supercapacitors are typically fabricated from a combination of an active material and a polymeric binder so called composite electrodes. Drop-casting a homogeneous mixture of an active material and a binder in a solvent is used to deposit this mixture onto the electrode, which is subsequently dried in an oven at a specific temperature (Arunkumar & Paul, 2017).

Composite electrodes combine carbon-based materials with conducting polymers or metal oxides or transition metal carbides and nitrides (MXenes) to form a single electrode capable of physically and chemically storing charges. Carbon-based materials have large specific surface areas and capacitive double charge layers, which improve the interface between the pseudocapacitive materials and the electrolyte. By using the Faradaic process, a pseudocapacitive material increases the capacitance of composite electrodes. Binary and Ternary composites are the two forms of composites that are now available. While ternary composites use three separate electrode materials to create a single electrode, binary composites only use two different electrode materials. Due to their high specific capacitance and low resistance, metal oxides offer another option for materials utilized in the construction of supercapacitor electrodes, making it easier to create supercapacitors with significant energy and power (Iro et al., 2016).

MXenes have a significantly higher pseudocapacitance than other capacitive materials when used as active materials in SCs. Ti_2CT_x and $Ti_3C_2T_x$ MXenes are being investigated as electrode materials for supercapacitors due to their capacity to store

charges via pseudocapacitive mechanisms. Because of the protonation of oxygen functional groups, the valence state of Ti bound to the surface oxygen groups switches continually, affording MXenes in the acidic electrolyte a remarkable pseudocapacitive charge storage capability (Babu et al., 2021).

Binder types also have an impact on supercapacitor performance. Binders play numerous essential functions in supercapacitor performance despite accounting for a small part of the electrode material (usually 2-5 percent of the mass in commercial electrodes) (Z. Zhu et al., 2016). Furthermore, the binder has a significant impact on the cycle life and rate performance of SCs. Binders for SCs should provide strong adhesion, disperse the active materials and conductive agent uniformly, and have high electronic and conductivity by holding together the active components, any conductive additive, and the current collector, ensuring all of these elements are in contact. (Guo, Wang, Zhang, & Han, 2020). Binder characteristics and concentration influence not just the dispersion behaviour of solid particles, but also the electrode's electrical conductivity. The inclusion of dispersing polymeric binders at the proper concentrations and particle to binder ratios results in homogenous particle distribution and the creation of a conducting network, which improves electron transport kinetics (Gordon, Kassar, & Willenbacher, 2020). Binders should also be environmentally friendly and inexpensive.

With all of the roles that binders play in an electrode (and the whole SCS), there are numerous desirable features in a good binder. Polyurethanes (PU) are a flexible type of polymer binder that comes in a variety of forms, including water-based PU, which is a colloidal system made up of PU particles dispersed in water. PU can have a wide range of functional groups, including urethanes, aliphatic hydrocarbons, esters, ethers, and urea, allowing it to be easily chemically or physically integrated with other polymers.

There are various advantages to using PU as a hybrid aqueous binder. First, PU has higher elasticity, tensile strength, and adhesion than common aqueous binders such as CMC, PAA, or poly (ethylene glycol) (PEG) due to its segmented structure with hard and soft domains; it can also form hydrogen bonds and physically crosslinked networks with these polymers to enhance their mechanical properties. Secondly, because PU contains a lot of polar groups, like urethane and carboxyl groups, PU can aid to reduce the shuttle effect in SCs. Loeffler et al. improved the electrochemical stability of oxide-based cathodes by using PU with CMC as a binder (Cholewinski et al., 2021).

1.2 Problem Statement

Despite significant advancements in other supercapacitor components, new study shows that the choice of binder is critical in stabilizing the cycle efficiency and mechanical qualities of the electrodes. Because the binder held the active components and the conductive filler with the current collector together, the device worked as intended (Jurado, Ibarra, Morales-García, Viñes, & Illas, 2021). To obtain certain qualities, the active ingredient must be mixed with a specific polymeric binder. Polyurethane (PU) was used as binder as materials in electrode preparation because PU is elastic, sticky, and porous, it allows for constant contact between electrodes and separator in order to secure the ion channel in a dynamic situation (Zhai et al., 2020). Therefore, the addition of PU would be a viable material in the possible applications including energy storage.

Because of its unique chemical and polymeric composition, PU has a two-phase microstructure with hard and soft parts. The hard domains provide PU its mechanical strength through hydrogen bonding at the urethane group's terminal, whereas the soft domains give PU its flexibility and elastic properties (Park, Park, Park, & Lee, 2017).

As a stretch-resistant binder, PU binder is an excellent choice for active materials (Rajendran, Mohan, Jayaraman, & Nakagawa, 2019). PU has been shown to be acceptable for usage binder because of its unique characteristic (Kwon et al., 2021).

Titanium carbide (TiC) electrodes have long ion transport paths because of the stacking nature of 2D materials, which makes them very slow at transferring ions. This makes a thick electrode very slow at transferring ions. When TiC is used to power electronic devices that require high area energy densities at rapid rates, the electrodes must be thick enough to store a large amount of charge. In this case, the issue of ion transport is more important because the low-rate performance will get worse with the thickness of the film (Lin et al., 2016). PU is needed to provide the dispersibility in liquid mixture, flexibility, and stable networks of the TiC electrode. Hence, the study for phase identification and surface morphology of TiC electrode at different percentage composition of PU (wt%) need to be investigate which PU (wt%) at 2, 4, 6,8, 10 wt%. Also, characterization of the electrochemical properties of TiC-PU-AC supercapacitor are needed to identify electrochemical property and analyze performance and specific capacitance of the supercapacitor.

1.3 Research Objectives

The objectives of this study are:

- i. To identify the phase identification of TiC electrode at different weight percentage of PU binder.
- ii. To perform characterization on the surface morphology of TiC-PU electrode.
- iii. To analyse the electrochemical properties and cycle life performance of TiC-PU based electrode as supercapacitor.

1.4 Thesis Outline

This research involved the mixture of PU materials from different composition in electrode slurry mixture of TiC, AC in NMP for SCs application. In this research, there are five parts that explain briefly every part involved with this research.

The first chapter are about introduction, problems statement and objectives of this study. Next, Chapter two are present about literature review on MXene electrode specifically TiC, PU as binder. Also, basic concept regarding physical and electrochemical characterization of PU usage in SCs application. Chapter 3 will cover on materials, chemicals, sample preparations and characterization that involved in this study.

Furthermore, Chapter 4 will present about all results of this study including morphological analysis, structural characterization and electrochemical characterization such as galvanic charge-discharge characterization, cyclic will be presented and discussed in details for further understanding. Finally, Chapter 5 will summarize and conclude the whole study from this project including the results and recommendations for future development.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This chapter introduced Titanium Carbide (TiC) or MXenes as active materials and Polyurethane (PU) as the potential electrode binder material for supercapacitor application. The properties TiC and PU and mechanism of supercapacitors are briefly discussed in this chapter. Various characterization techniques were also conducted in this study including materials characterization for phase, morphology and structural analysis and electrochemical characterizations.

2.2 MXenes

Active materials in SCs are selected according on the intended application, since differing intrinsic qualities might maximize a certain parameter. With example, if a material has a high active surface area that is accessible to electrolyte ions, it will contribute significantly to the electrical double-layer capacitance. This is often the case for carbon-based materials like graphene. However, this is inadequate to meet the demands of future microelectronics, which need high energy output from a compact footprint. To enhance the energy density of SCs, transition metal dichalcogenides and transition metal oxides such as MXenes are utilized (Das & Wu, 2020).

Two-dimensional (2D) transition metal carbides and nitrides, or MXenes, are found in great chemical abundance. Intriguing new possibilities presented by MXenes' intrinsic electrical conductivity, enhanced hydrophilicity, complex surface chemistry, and layered structure have resulted in a significant rise in the number of articles devoted to these materials in SCs application. However, they lack the high electrical conductivity of carbon, necessitating the use of carbon-based binder or current

collectors to improve their rate performance for SCs. MXene, as a 2D material, has a large surface area that provides electrical double-layer capacitance. Simultaneously, it greatly increases pseudo-capacitance via an intercalation mechanism that accommodates a wide range of cations. MXene has emerged as a great solution to this problem in this regard. As a result of their high energy density and low manufacturing complexity, SCs in particular are a promising application for MXenes. (Hu et al., 2020).

2.2.1 Structure and properties of MXenes

Wet etching of MAX phases is the main step in the synthesis of an MXenes. The M atoms are packed in a hexagonal close packing (hcp) lattice, and the X atoms fill the octahedral interstices between them; these layers are sandwiched between A-group element layers with a space group of $P6_3/mmc$. With the A layers removed, the remaining $M_{n+1}X_n$ layers take on a 2D close packed hexagonal structure, with O, OH, F, H, and/or Cl atoms attached. The higher negative formation energy of surface terminations bonding with the outer transition metal layers, as well as the positive phonon frequencies of fully terminated MXenes, have demonstrated that MXenes are always fully terminated (Lee & Kim, 2019).

As shown in Figure 2.1 a, the three most common configurations for functional group terminated MXenes are type I, all functional groups are located above the hollow site of three neighboring X atoms and point to the M atoms in the second Ti atomic layer; type II, all functional groups are located on top of the topmost sides of the X atoms; and lastly type III, a combination of types I and II, where one functional group is located on top of the hollow site of For most MXenes, type I has been calculated to be the most stable configuration. MX layers with a single surface group termination are stacked to create a layered structure in MXene. Based on the relative position of MX

layers with terminations shown in Figure 2.1 b, they are arranged in two stacking types, namely simple hexagonal (SH) and Bernal stacks, and are connected by dihydrogen bonding between the surface groups (Hu et al., 2020).

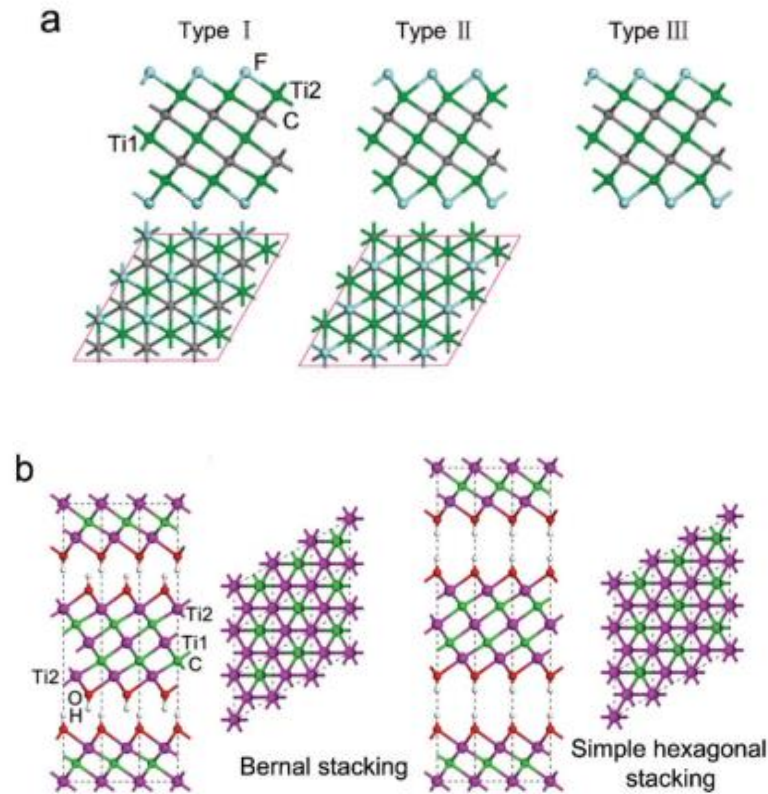


Figure 2. 1 (a) Structure configurations of Ti₃C₂F₂ with different arrangements of the surface F atoms from side views and top views, (b) Projections of two distinct Ti₃C₂(OH)₂ stacking types (Hu et al., 2020).

2.2.2 Titanium Carbide

In 2011, the first member of MXenes, Titanium Carbide (Ti₃C₂T_x), is the first reported and most studied MXene for supercapacitor application (Tang et al., 2021).

2.2.2(a) Properties of Titanium Carbide

Titanium carbide (Ti₃C₂) electrodes have been demonstrated to have exceptionally high volumetric capacitances among MXenes. The proton-induced

pseudocapacitance, it exhibits in acidic aqueous electrolytes is very high. $\text{Ti}_3\text{C}_2\text{T}_x$ has great electrical conductivity (up to $15,000 \text{ S cm}^{-1}$), high packing density (up to 4 g cm^{-3}), high pseudocapacitance as well as ultrahigh volumetric capacitance ($\approx 1,500 \text{ F cm}^{-3}$). Thus, $\text{Ti}_3\text{C}_2\text{T}_x$ is a superior electrode material for supercapacitors compared to other electrode materials. (Dhamodharan et al., 2022).

For SCs application, according to M. R. Lukatskaya et al., the flexible Ti_3C_2 films have a volumetric capacitance of over 300 F cm^{-3} at a scan rate of 2 mV s^{-1} and outstanding cycle stability. (Lukatskaya et al., 2013). In addition, a study found that Ti_3C_2 /polymer composites had a remarkable volumetric capacitance of 530 F cm^{-3} at 2 mV cm^{-1} (Ling et al., 2014) and M. Ghidui et al. reported on study on manufacturing for additive-free films of Ti_3C_2 'clay' by a simpler approach, and the films had volumetric capacitances of up to 900 F cm^{-3} at 2 mV s^{-1} (Ghidui et al., 2014). Additionally, M.-Q. Zhao et al. exhibited a considerable increase in volumetric capacitance which are 390 F cm^{-3} and outstanding rate performance of sandwich-like $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$ electrodes (Zhao et al., 2014). However, the impact of Ti_3C_2 bulk loading on electrochemical performance has not yet been investigated (Lin & Zhang, 2015).

2.2.2(b) Application of Titanium Carbide

MXenes have been successfully used in electrochemical energy storage. One of the most noteworthy applications for MXenes is supercapacitors. Prior to this study, only a few papers on MXene and polymer composites as an electrode material for supercapacitor applications have been reviewed.

After that, Sixing Xu et al presented a micro supercapacitor (MSC) based on MXene thick interdigital electrodes and Micro-electromechanical systems (MEMS) technology. The increased mass loading was achieved by using $300 \mu\text{m}$ thick titanium

carbide as interdigital fingers and polymer electrolyte (PE) as electrodes. The findings reveal a specific capacitance of 276 mF cm^{-2} and a capacitance retention of 95% after 1000 cycles. (Garg et al., 2020).

Furthermore, there was study where MXene-Ti₂C-based electrode with a gravimetric capacitance of 450 F g^{-1} at a scan rate of 1 mV s^{-1} was discovered, whereas Ti₃C₂ has even higher values. Generally, both Ti₂C and Ti₃C₂ have a layered electrochemically active surface that may be exploited for high-capacitance charge storage that good for SCs (Johnson et al., 2019).

2.3 Polyurethane Materials

Binders are inactive components since they do not directly contribute to cell capacity. However, their importance in electrode processing and impact on electrode performance have been thoroughly discussed (Eshetu & Figgemeier, 2019). Binder material qualities include thermal, chemical, and electrochemical stability, tensile strength (strong adhesion and cohesion), flexibility, and viscosity (of the slurries) (Lingappan, Kong, & Pecht, 2021). Using a binder helps to construct stable networks of solid electrode components, such as active materials and conductors (cohesion). The binder must also keep the composite electrode near to the current collector (adhesion) (Loeffler, Kopel, Kim, & Passerini, 2015). Polymer also can be direct as a kind of encapsulation for supercapacitors (K. Wang, Zhao, Zhou, Wu, & Wei, 2011). To keep active materials from peeling off and maintain their charge storage capacity when bent or twisted, highly sticky binders may be an option (J.-A. Wang, Lin, Wang, Ma, & Hu, 2019).

According to previous literature review and research, that Polyurethane (PU) binder exhibits excellent mechanical stability to electrode even when folded because a

slurry containing an equivalent amount of PU produced a smooth electrode free of cracks and the film detached easily from the substrate. Additionally, conductivity increases as the binder content decreases. According to Liu et al., free polymer that is not immobilized on the surface of conductive carbon or active material has a significant influence in defining the electrodes' electric conductivity (Park et al., 2017). Additionally, PU has stretchability, stickiness, and porosity allow it to maintain electrical contact with the separator when in a dynamic condition, thereby preserving the ion pathway (Zhai et al., 2020). Therefore, adding PU would be a promising material in the potential energy-storage applications.

2.3.1 Properties of Polyurethane

The urethane group is the most common repeating unit in PUs, and it is formed by reacting alcohol ($-OH$) with isocyanate (NCO) (Amran et al., 2021; Zia, Ahmad, Anjum, Zuber, & Anjum, 2015). Ethers, esters, urea, and some aromatic chemicals are among the other groups found in PUs. Because of the diverse materials from which they can be synthesised and their diverse applications, PUs are classed as stiff, flexible, thermoplastic, waterborne, binders, coatings, adhesives, sealants, and elastomers (Akindoyo et al., 2016). Simply described, polyurethanes are polymers whose primary chain contains urethane groups ($-NH-CO-O-$) (Xu, 2014).

Macro-diol (functional group $-OH$) and di- or polyisocyanate (functional group $-NCO$) are the two basic components of PU (Muzaffar, Bhatti, Zuber, Bhatti, & Shahid, 2016). These two functional groups combine to create lengthy chains and networks that are joined by an exothermic urethane link ($-O(CO) (NH)-$) (Karak, 2017). PU can be synthesised to have a wide range of mechanical qualities to meet application needs. In order to make PU, the polyol, diisocyanate, and chain extender are all necessary.

Mechanical and physical qualities can be greatly influenced by the polyols and diisocyanates employed in the PU process (Somarathna, Raman, Mohotti, Mutalib, & Badri, 2018).

The unique behaviour of thermoplastic elastomers is caused by their morphology: covalent crosslinks are replaced by virtual crosslinks (Y. Li, Luo, & Hu, 2015). Virtual crosslinking occurs when a dispersed hard phase (urethane or urea groups) is contained within a soft phase (a polyol or polyester, for example) (Jin, Guo, You, & Tan, 2020) These virtual crosslinks are formed by hydrogen bond interactions between the C=O and N–H groups in the urea or urethane groups in the hard segments (Oprea, 2005).

PU is made by adding diisocyanates $R^1(-NCO)_2$ and polyols $R^2(-OH)_n$ together as shown in Figure 2.2. It is known for having the urethane group NH-(CO)-O (Gama, Ferreira, & Barros-Timmons, 2018; Schneidermann et al., 2019). There are a wide range of monomers in these compounds that can be used to make polyurethane materials, including aliphatic and aromatic isocyanate components (R^1) (Malik & Kaur, 2018) and a variety of various dihydric or polyhydric alcohols (R^2) (Lee, Min, & Lee, 2019). Because there are several monomers available, new functional groups can be added to the PU framework and reaction conditions or specific properties can be adjusted, such as ensuring that the polymer chains remain stable and fast via aromatic isocyanates (Schneidermann et al., 2019).

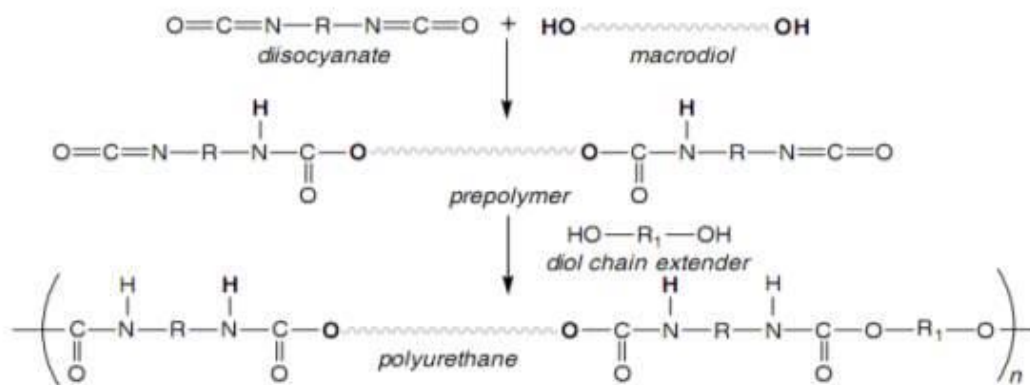


Figure 2. 2: Method of synthesis of thermoplastic polyurethane (Fuensanta & Martín-Martínez, 2020).

2.3.2 Application of Polyurethane

An article was identified that demonstrated the use of PU/CMC as a binder for SCs electrodes. After thermal cross-linking, the PU is thermally stable up to 170°C in a nitrogen atmosphere and has improved electrochemical stability in a potential range of 0.02 V to 5.00 V, allowing electrolyte ion crossing. It is also shown that the PU encapsulates lithium nickel manganese cobalt oxides (NMC), which are employed as active material particles during the electrode slurry forming and coating, significantly decreasing corrosion of the cathodic (aluminum) current collector. Cycle stability and discharge capacity of the cathode electrodes are improved with increasing PU binder content, demonstrating a desirable property for SCs (Loeffler et al., 2015).

Additionally, a flexible and wrinkle-free electrode for flexible SCs was fabricated using a PU binder by casting a slurry on a glass substrate and detaching the resulting film after drying. The energy density of the PU-based electrode (430 W h kg⁻¹) is equivalent to that of another kind of polymer binder, Polyvinylidene Fluoride (PVDF)-based electrode (360 W h kg⁻¹), and it decreases with increasing PU binder percentage, indicating that the PU-based electrode is ideal for SCs. (Park et al., 2017).

2.4 Supercapacitor

SCs fill the void between traditional electrolytic capacitors and batteries. This is an example of a capacitor that has been electrochemically charged. The fundamental equations used to describe capacitors are the same in the case of supercapacitors, but the energy storage mechanism is different. Various electrode-active materials, including as activated carbon, mesoporous carbon, carbon nanotubes, graphene, and others, are always used in high-performance supercapacitors. SCs employ both aqueous and organic electrolytes, however only organic electrolyte-based supercapacitors are capable of delivering high voltage. Nevertheless, aqueous electrolyte-based supercapacitors have a longer cycle life than organic ones. Figure 2.3 depicts the conceptual distinction between capacitors and supercapacitors, which are two of energy storage systems. Table 2.1 provides a comparison between conventional capacitors and SCs in order to facilitate comprehension (Banerjee et al., 2020).

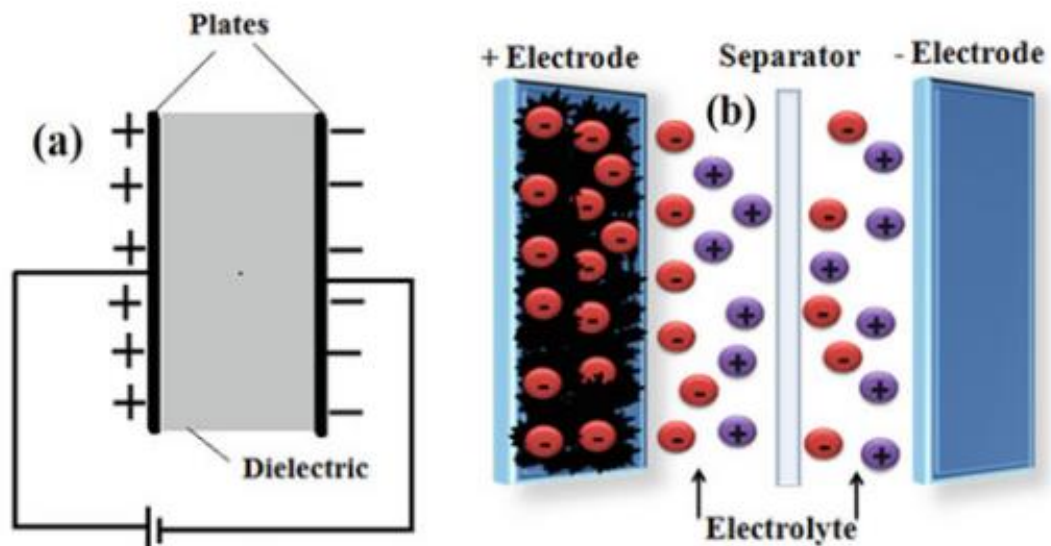


Figure 2. 3 Schematic of (a) capacitor and (b) supercapacitor (Banerjee et al., 2020).

Table 2. 1 Comparative analysis of conventional capacitors and supercapacitors..

Characteristic	Capacitor	Supercapacitor	References
Component	Conducting plates, dielectric material	Electrodes, electrolyte, separator, current collector	(Banerjee et al., 2020, Hegg & Mamishev, 2022).
Charge stored	Between charged plates	Interface of electrode and electrolyte	
Charging time	10^{-3} to 10^{-6}	1s to 30s	(Gautham Prasad et al., 2019)
Discharging time	10^{-3} to 10^{-6}	1s to 30s	
Specific Energy (W h kg ⁻¹)	< 10^{-1}	< 10^{-2}	(Riaz et al., 2021)
Specific Power (W kg ⁻¹)	<1000	500-10000	(Banerjee et al., 2020).
Life time(Cycles)	10^6 to 10^8	10^6 to 10^8	(Iyer & Hegde, 2015)

SCs are being researched and widely acknowledged as a potential energy storage technology due to their desirable qualities, such as high power density and high recyclability. Despite their low energy density, they possess other advantages like as low internal resistance, a broad operating temperature range, and excellent efficiency. These advantageous characteristics make them ideally suited for use alone or in conjunction with other high-energy devices for sinking/sourcing power in real-world facilities (Zhang et al., 2018).

2.4.1 Component of supercapacitors

There are two types of supercapacitors: two-electrode and three-electrode. To evaluate the electrochemical properties of electrode active materials, researchers usually use a three-electrode configuration (K. Wang et al., 2021). Three-electrode SCs arrangement with working electrode (WE), reference electrode (RE), counter electrode (CE), and electrolyte (Petrić & Mandić, 2021; Raccichini, Amores, & Hinds, 2019; Toudjine, Boulkadid, Trache, Belkhiri, & Mezroua, 2022). Active materials are either coated on or used directly as the working electrode. Supercapacitors have two (2) components: active components and passive components (Mathis et al., 2019). The general structure of SCs can be observe in Figure 2.4.

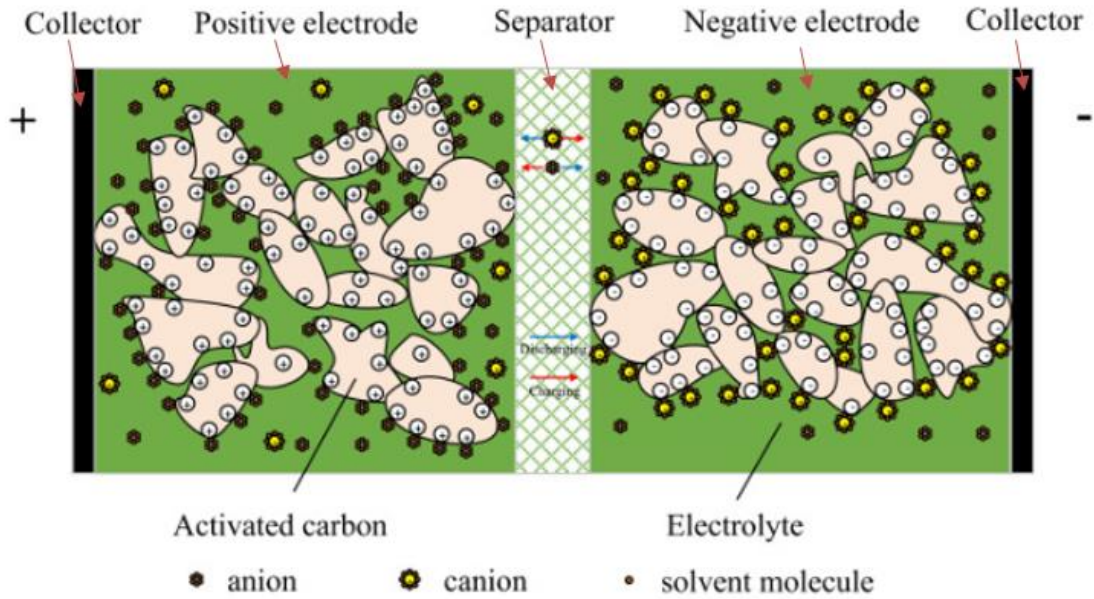


Figure 2. 4 Structure of supercapacitor (Zhang et al., 2018)

Carbon-based or conductive materials (such as carbon nanotubes (CNTs), activated carbon materials (ACs), and graphene), transition metal oxides as active materials (such as ruthenium oxide (RuO_2), manganese oxide (MnO_2), and nickel oxide NiO), and conducting polymers or polymer binder (such as polyaniline (PANI), polythiophene (PTh), and polypyrrole (PPy)) are the three main categories of electrode materials. MXenes are a realistic potential in the realm of energy storage, notably as electrodes for supercapacitors, due to their uncommon combination of hydrophilicity and metallic conductivity (K. D. Verma et al., 2020).

In commercial cells, a metal substrate (Cu foil, Al foil, Ni foam, etc.) is commonly utilized as a current collector. The metal substrate is then spread-coated with a slurry including the active ingredient, binder, and conductive additives. This method is simple and effective; nevertheless, the non-conductive and inactive binder reduces the electrical conductivity and specific capacity of the electrode, and the metal current collector increases the total weight of the electrode (Ji et al., 2015). In the typical process of preparing electrodes, a nonconductive polymer binder is utilised, which

results in an increase in interface resistance and a decrease in the number of material active sites (Mastragostino, Arbizzani, & Soavi, 2002).

Binders are inactive components since they do not contribute directly to cell capacity. Their significance in electrode processing and impact on electrode performance, on the other hand, has been comprehensively addressed (Eshetu & Figgemeier, 2019).

2.4.2 Types of Supercapacitors

There are three types of supercapacitors: The Electrochemical Double Layer Capacitor (EDLC), the Pseudocapacitor, and the Hybrid type generated by a combination of the EDLC and pseudocapacitor (Shafiei et al., 2021).

The components of an EDLC capacitor are shown in Figure 2.5. The charge accumulator is located at the contact point between the electrode and electrolyte, as shown in Figure 2.2. When a supercapacitor is charged, electrons are transferred from the negative to the positive electrode through the external loop. Figure 2.5 shows that cations in the electrolyte go toward the negative electrode, whereas anions move in the opposite direction, toward the positive electrode. But during the discharge process, the electrons and ions move in the other way. An EDLC supercapacitor does not allow for charge transfer (Okonkwo et al., 2017).

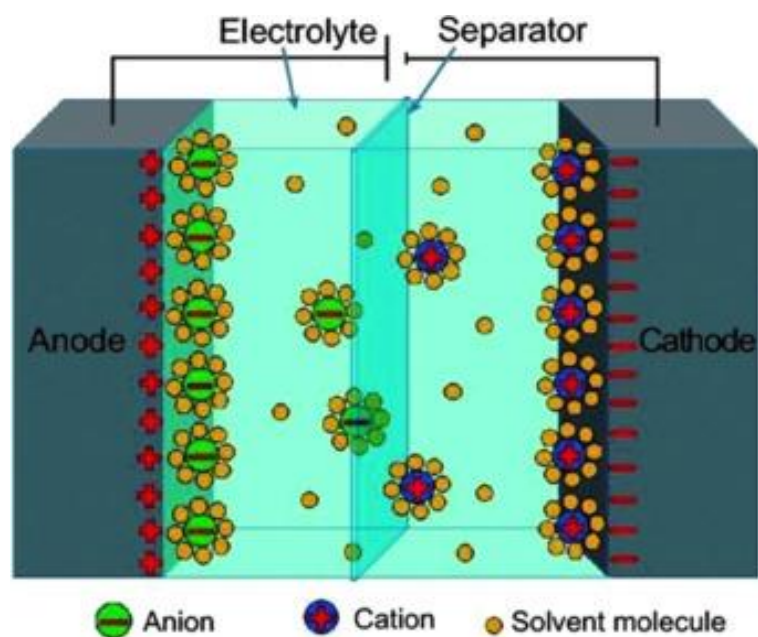


Figure 2.5 Schematic representation of an EDLC (Muzaffar et al., 2019).

As depicted in Figure 2.6, pseudocapacitors, also known as faradaic supercapacitors, differ from EDLCs in that pseudocapacitance is generated by rapid and reversible faradaic processes (redox reactions) at or near the electrode surface. The supercapacitor cell receives and discharges a faradaic current as a result of faradaic electrochemical processes. Though these methods improve supercapacitors' energy density and specific capacitance in comparison to EDLCs, pseudocapacitors' low power densities and poor cycle stability make them less desirable. The most commonly used pseudocapacitive materials are metal oxides (such as RuO₂ and MnO₂) and electrically conducting polymers (such as polyanilines, polypyrroles, and polythiophenes) (Zhou et al., 2018).

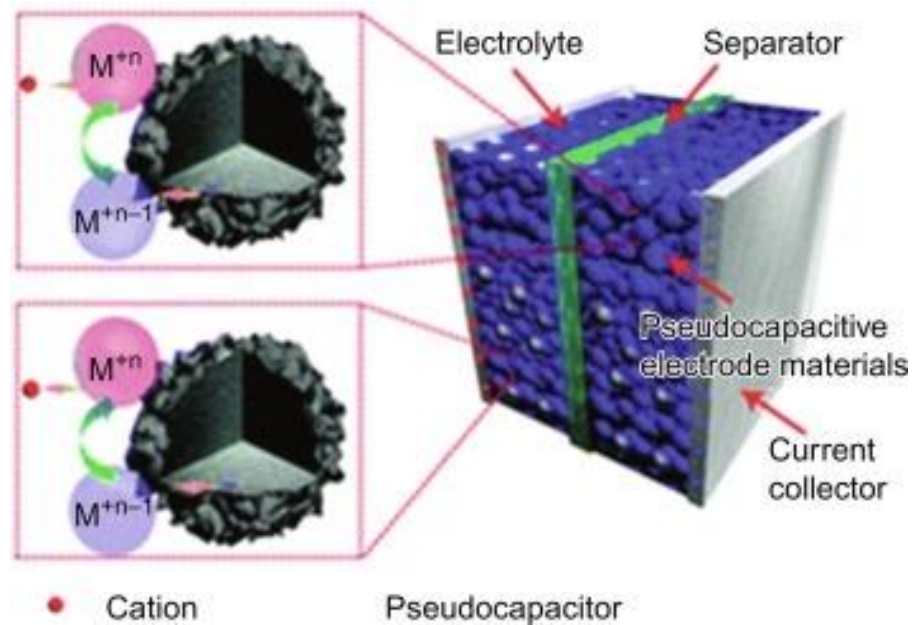


Figure 2. 6 Schematic representation of pseudocapacitors (Zhou et al., 2018).

In recent years, hybrid SCs with their better performance in energy density without modifying their power density have become popular. In comparison to standard EDLC and pseudocapacitors, the hybrid supercapacitor has a higher specific capacitance. Hybrid supercapacitors, a combination of an EDLC and a pseudocapacitor, typically exhibit an asymmetric behavior that serves to boost their capacitance. This asymmetric strategy represents a new beginning toward the much-required pollution-free, durable, and effective energy-storing performance (Damilola Momodu et al., 2021).

The hybrid SCs, which are composed of an EDLC and a pseudocapacitor, have better properties than the combined components. As shown in Figure 2.7 The intrinsic shell area and atomic charge partition length are used to store energy in EDLC. In contrast, energy storage in a pseudocapacitor is accomplished through rapid repeatable redox reactions between electro-active units resting atop active electrode material and an electrolyte solution. These two storage strategies are combined to provide the energy

storage mechanism of hybrid supercapacitors. The hybrid supercapacitor has one half that operates as an EDLC and the other half that functions as a pseudocapacitor. Hybrid SCs have better energy and power densities than ordinary EDLC and pseudocapacitors. This promotes their use in energy-efficient systems over other energy-storage technologies (Muzaffar et al., 2019).

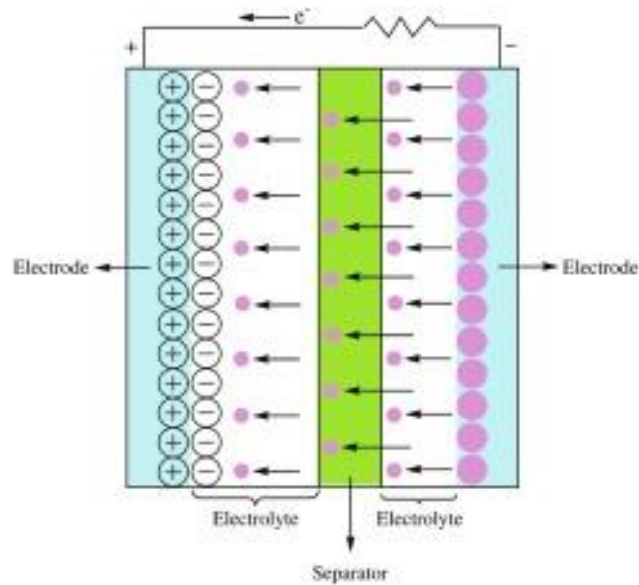


Figure 2. 7: Schematic representation of hybrid capacitor (Shafiei et al., 2021).

2.4.3 Application of Supercapacitors

SCs have several applications beyond the electronic sector, including those in hybrid electric vehicles and the distribution of electrical power. Current supercapacitors face two major flaws: inferior energy density and prohibitive cost. As a result, unique low-cost supercapacitors with great energy density should be created to meet society's demands. The current chapter examines Faradaic and non-Faradaic processes, supercapacitor kinds, structure (i.e., electrode, electrolyte, electrolyte membrane, and current collector), critical factors for performance estimate, electrochemical characterizations, and so on (Banerjee et al., 2020).

2.5 Physical properties

Some characterization techniques have been performed to identify structure and surface morphology PU materials in electrode mixture materials in SCs application.

2.5.1 Surface Morphology

The scanning electron microscope (SEM) is one of the most flexible tools available for examining and analyzing microstructure morphology and chemical composition characterizations (Zhou, Apkarian, Wang, & Joy, 2006). SEM generates a variety of signals on the surface of solid specimens using a focused beam of high-energy electrons (Akhtar, Khan, Khan, & Asiri, 2018).

SEM is an imaging technique that employs electrons. The incident electron beam is scanned across the surface of the sample in a raster pattern, and the backscattered or secondary electrons emitted are measured. When a cathode emits electrons in the presence of a very high electric field, it is referred to as a field emitter FESEM, which produces better images. Although sample preparation is straightforward, the electron beam might induce biological material degradation and so should only be utilized for limited samples (S. K. Verma, 2019).

Figure 2.8 shows SEM pictures of the samples. Waterborne polyurethane (WPU) particles in aqueous dispersion had a spherical shape with a diameter of approximately 20 μm (Jeong, Du, Kim, Raj, & Kim, 2019). Polyurethane-potassium poly(acrylate) (WPU-PAAK) is a sticky copolymer that serves as a binder (Palve, Mensah-Darkwa, de Souza, & Gupta, 2021) in the production of flexible, quasi-solid-state supercapacitor electrodes based on AC/CNT. Figure 2.8b shows the FE-SEM images of the AC/CNT@WPU-PAAK composites' surface morphologies. Dispersal of WPU-PAAK is easy due to the network structure and flexibility (J.-A. Wang et al.,