

Asymmetric Supercapacitors NP-MnO₂//P-MXene/C_{PAQ}-A Device in Aqueous Electrolyte with a Wide Voltage Window, Good Mechanical Flexibility, and High Circle Stability

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Abstract: This study presents the development of an asymmetric supercapacitor (ASC) utilizing NP-MnO₂ as the positive electrode and P-MXene/ C_{PAQ}-A (PAQ: quinone-amine polymer) as the negative electrode. This combination enhanced energy and power density by combining pseudocapacitive and electrochemical double-layer mechanisms. Characterization and electrochemical analysis reveal superior performance, including a wider voltage window (1.9V) and extended cycle life, positioning this kind of ASC as a promising solution for advanced energy storage applications. Environmental impact is minimized using water-based electrolytes.

Keywords: Asymmetric supercapacitor, MXene, NP-MnO₂, micro-supercapacitor

1. Introduction

The global energy crisis from rapid industrialization and urbanization increases our reliance on non-renewable energy sources. This dependence has increased environmental issues such as water pollution and global warming, highlighting the urgent need for sustainable energy solutions[1], [2]. Technologies like second-time batteries and supercapacitors, which can be recharged multiple times, represent a significant advancement in this area[3]. These innovations and progress in green energy are crucial in addressing the inefficiencies and environmental impacts of traditional fossil fuels.

The energy storage landscape is diverse, with each type of battery possessing unique strengths and weaknesses. Traditional batteries, such as lithium-ion batteries, are mainly in modern energy storage because of their high energy density. That means the traditional battery stores large amounts of energy in a compact form. They find extensive applications in consumer electronics, electric vehicles, and renewable energy systems.

However, they also suffer from drawbacks such as lengthy charging times, limited cycle life, and potential environmental and safety risks due to using flammable electrolytes and rare metals[3], [4], [5]. In contrast, supercapacitors, or electrochemical double-layer capacitors (EDLCs), offer swift charge-discharge cycles and deliver high power density but typically provide relatively low energy density. Because EDLCs store charge electrostatically at the electrode-electrolyte interface without

involving chemical reactions, they can deliver high power density and extensive cycle life, albeit with modest energy density.[6]. On the other hand, pseudo capacitance involves faradaic processes, storing charge through reversible redox reactions, which result in higher energy density than EDLCs but with moderate power density and a shorter cycle life[7]. Asymmetric supercapacitors (ACS) combine electrochemical double-layer capacitor (EDLC) and pseudocapacitance mechanisms by using carbon-based materials for one electrode and metal oxides or conducting polymers for the other. This asymmetric system enhances energy density while maintaining high power density, offering a promising solution that bridges the gap between batteries and capacitors[8]. ACS presents a balanced trade-off between energy and power density, making them suitable for applications requiring quick energy delivery and moderate energy storage[8]. They offer several distinct advantages for energy storage, including enhanced energy density by combining the high energy storage capabilities of batteries with the high-power density of capacitors, allowing for a wider voltage window and greater energy storage within the same device footprint[9]. ACS benefits from fast charging and discharging capabilities, essential for applications requiring quick energy bursts. They typically exhibit longer cycle lives, improving durability and reducing maintenance needs[8]. The use of more abundant and cost-effective materials, coupled with increased safety under thermal stress and overcharge conditions, makes ACS particularly effective for a broad range of applications[10].

The supercapacitor electrode materials consist of a wide variety, including two-dimensional materials, which offer high EDLC stemming from their thin-sheet nanostructures, and transitional metal compounds, which generate Faradaic capacitance through robust redox pairs[8].

MXenes, rising 2D materials, can be simplified as $M_{n+1}X_nT_x$ ($n=1,2,3,4,\dots$). M reprints early transition metal, X means carbon or nitrogen, and T_x means the surface terminal groups[11], [12], [13]. MXene materials like $Ti_3C_2T_x$ offer several key advantages for supercapacitor applications, including high metallic conductivity that facilitates rapid electron transfer, a large specific surface area for enhanced charge storage, and inherent hydrophilicity which improves interaction with aqueous electrolytes and ion transport[14]. Their flexible layered structure supports the intercalation of various ions, allowing customization for specific uses, while their chemical versatility enables surface modification with functional groups such as $-O$, $-OH$, $-F$, and $-Cl$ to tailor electrochemical properties[15].

On the other hand, NP- MnO_2 offers several advantages for use in asymmetric symmetric supercapacitors, including exceptional energy storage capabilities and outstanding cyclic stability, which supports its durability in long-term applications[16], [17]. It operates over a wide potential window, enhancing its utility across various applications by increasing the energy density[18]. Additionally, NP- MnO_2 achieves high specific energy and power densities, illustrating its efficiency in delivering robust energy output and rapid charging capabilities[19]. Its environmental compatibility further enhances its appeal, being both cost-effective and non-toxic, making NP- MnO_2 an excellent material for advancing the performance and sustainability of energy storage technologies[20].

In this paper, a new kind of asymmetric micro supercapacitor is fabricated. The asymmetric supercapacitor, combining P-MXene/ C_{PAQ} -A as the negative electrode and NP- MnO_2 as the positive electrode, offers several advantages for advanced energy storage. This configuration leverages the high electrical conductivity of P-MXene/ C_{PAQ} -A for rapid charge and discharge capabilities, while the pseudocapacitive properties and porous structure of NP- MnO_2 enhance ion diffusion and energy density. A sulfuric acid electrolyte ensures high ionic conductivity and chemical stability, improving the device's longevity and reliability[21]. Additionally, the flexible nature of P-MXene/ C_{PAQ} -A supports applications in flexible electronics, making this supercapacitor ideal for technologies requiring robust, high-performance energy storage that balances quick energy delivery with sustained output[22].

This specific innovation is part of a broader category of micro-supercapacitors, which offer a range of advantages crucial for miniaturized and flexible electronic applications. These devices provide extremely high power densities that support rapid charge and discharge rates essential for instant power delivery. Their compact size facilitates seamless integration into microelectronic devices and wearable technology, enhancing device portability without compromising performance. Additionally, they can be fabricated on flexible substrates, making them adaptable to various forms and conducive to integration into smart textiles. Micro-supercapacitors also exhibit long cycle lives, ensuring sustained performance over thousands to millions of cycles, and demonstrate robust environmental stability, maintaining functionality across diverse conditions such as temperature fluctuations and mechanical stress. These features make them particularly valuable for developing advanced, energy-efficient electronic devices where size, flexibility, and durability are paramount[23], [24], [25].

The newly developed asymmetric supercapacitors (ACS), particularly the NP- MnO_2 //P-MXene/ C_{PAQ} -A electrodes represent a significant advancement in addressing the limitations traditionally associated with supercapacitors. These new ACS designs markedly enhance overall energy storage capacity by integrating the high energy density characteristics of pseudocapacitors with the power density benefits of Electric Double-Layer Capacitors (EDLCs)[26]. This asymmetric design preserves the rapid charge and discharge capabilities and substantially increases energy density, making these capacitors suitable for a wide range of applications. The combination of these two types of capacitors allows for both benefits to be realized, leading to improved performance in various scenarios where quick energy storage and release are crucial.

A key improvement introduced by these ACS designs is the expansion of the voltage window. Traditional supercapacitors are often limited by a narrow voltage range, directly restricting their energy capacity[27]. However, the NP- MnO_2 //P-MXene/ C_{PAQ} supercapacitors utilize advanced materials and innovative electrode designs that allow for a significantly larger voltage window, ranging from -0.6V to 0.3V for the negative electrode[28] and from 0V to 1.0V for the positive electrode[29]. This results in an overall voltage window of 1.9V, a substantial increase compared to conventional designs. This broader voltage window directly translates to higher energy storage per unit volume, making these capacitors more efficient and versatile, particularly in applications that require high voltage.

Beyond the improvements in energy density and voltage range, these new ACS designs also address several other critical issues in traditional supercapacitors. The NP- MnO_2 electrode, for example, incorporates nanostructural porous manganese oxide, which significantly enhances specific capacitance compared to conventional materials like activated carbon. This enhancement in capacitance leads to greater energy storage, which is vital for applications requiring sustained power delivery[30], [31]. Additionally, the P-MXene/ C_{PAQ} -A electrode improves conductivity using MXene, a material known for its excellent electrical properties. This improvement addresses the common issue of low conductivity in traditional supercapacitors, thereby increasing the overall power density and performance of the device[32], [33].

Moreover, these ACS designs exhibit remarkable cycling stability, maintaining high capacitance retention of more than 90% with the whole of the coulombic efficiency after 10,000 cycles, this longevity ensures that the supercapacitors remain reliable over extended periods of use, making them more suitable for long-term applications[29]. Finally, by employing materials such as manganese dioxide, which are both abundant and environmentally friendly, these supercapacitors offer a more sustainable and cost-effective solution compared to traditional designs. This sustainability aspect is crucial in the modern push towards greener and more efficient energy storage technologies.

2. Experiments

2.1. Design potential experiments, including synthetic method

Materials: A variety of reagents and materials were employed in this work. These included lithium fluoride (LiF); titanium aluminum carbide (Ti_3AlC_2 , $\geq 99\%$); poly(methyl methacrylate) (PMMA); o-phenylenediamine (97%); p-benzoquinone (99.5%); polyvinylpyrrolidone (PVP, average molecular weight $\sim 40,000$); 2-thiophene methanol (97%); resorcinol (99%); formaldehyde solution (37 wt% in H_2O); concentrated sulfuric acid (H_2SO_4 , 95–98%); and a polypropylene separator (PP coated 3501).

Additional compounds included potassium hydroxide (KOH, analytical grade, sourced from Guangdong Chemical Engineering-Technological Reagent and Development Center); activated carbon (AC); a polytetrafluoroethylene (PTFE) binder (60 wt% in water, D210C); and ammonia solution (28%, from the same Guangdong supplier). Other materials were multi-walled carbon tubes with $< 5\%$ metal oxide (TGA), NC-31000, manganese (II) acetate tetrahydrate (anhydrous), and N-methyl-2-pyrrolidone (NMP, 99.5%). Pellets composed of polyvinylidene fluoride (Mw $\sim 530,000$) were also used.

Both activated carbon and absolute ethanol (both manufactured in the USA) were utilized as received without further purification.[28], [29]

2.2. Synthesis of P-MXene/ C_{PAQ} -A electrode

Based on the procedure outlined by Rui et al[29], the synthesis of the P-MXene/ C_{PAQ} -A electrode involved, begins by mixing 1 g of Ti_3AlC_2 with 30 mL of a 9 M HCl solution containing 1.98 g of LiF. Stir this mixture at 40°C for 45 hours. After this reaction period, wash the resulting mixture with deionized water using repeated centrifugation at 3500 rpm for 5 minutes per cycle and decantation until the pH of the supernatant exceeds 6. This process yields a multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the solution. Following the final centrifugation, the sediment is collected and redispersed in 300 mL of deionized water. Deoxygenate this suspension by bubbling argon through it for 30 minutes, then sonicate it in an ice bath for 1 hour at room temperature under an argon flow, followed by another round of centrifugation for 1 hour at 3500 rpm. The obtained dark green supernatant contains several layers of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes that are ready for electrode fabrication. For electrode preparation, mix the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene suspension with anhydrous ethanol in a 3:1 volume ratio and stir for 10 minutes. Add PMMA nanospheres to this mixture and stir for an additional 30 minutes. To create the P-MXene/ C_{PAQ} -A electrode, add p-benzoquinone to the mixture until fully dissolved, then introduce o-phenylenediamine in a 1:3 molar ratio to p-benzoquinone, and continue stirring for 30 more minutes. For the P-MXene/CResin-A electrode, dissolve resorcinol in the MXene and PMMA solution, add formaldehyde, and stir. Then add ammonia to adjust the solution to a concentration of 0.1 mol/L, ensuring the mixture's resorcinol to formaldehyde mass ratio is 2:3. For the P-MXene/CPVP-A electrode, incorporate a 2% PVP solution into the MXene and PMMA solution at a 0.3:1 solid mass ratio. Similarly, for the P-MXene/CPTH-A electrode, add 2-thiophene methanol in a 15% acetonitrile solution at the same solid mass ratio. Form a film by filtering a known volume of the prepared solutions through a polypropylene membrane. Transfer the film with the membrane into a KOH solution and soak for 2 hours. After this alkali treatment, dry the film at room temperature and carefully peel it off the membrane. For the final step, treat the P-MXene/CPVP-A electrode film at 280°C under flowing argon for 2 hours for stabilization and then anneal at 400°C for 4 hours with a heating rate of 5°C per minute. The other electrode films—P-MXene/ C_{PAQ} -A, P-MXene/CResin-A, and P-MXene/CPTH-A—are directly annealed at 400°C under the same conditions. Adjust the film

thickness by varying the volume of the solution used in the filtering step. This careful control of the process parameters ensures the synthesis of high-quality supercapacitor electrodes[29].

The synthesized P-MXene/ C_{PAQ} -A material that is self-supporting is used directly to form the electrodes do not require additional adhesives or conductive additives. This simplifies the electrode fabrication and maintains the purity and performance of the electrode. These electrodes are then assembled into a supercapacitor device where the P-MXene/ C_{PAQ} -A serves as the negative electrode [30].

The figure below illustrates the step-by-step synthesis of self-supporting P-MXene/C composite electrodes starting from a layered Ti_3AlC_2 MAX phase (shown in purple), which is etched with a LiF/HCl mixture to remove the Al layers and yield $Ti_3C_2T_x$ MXene nanosheets.

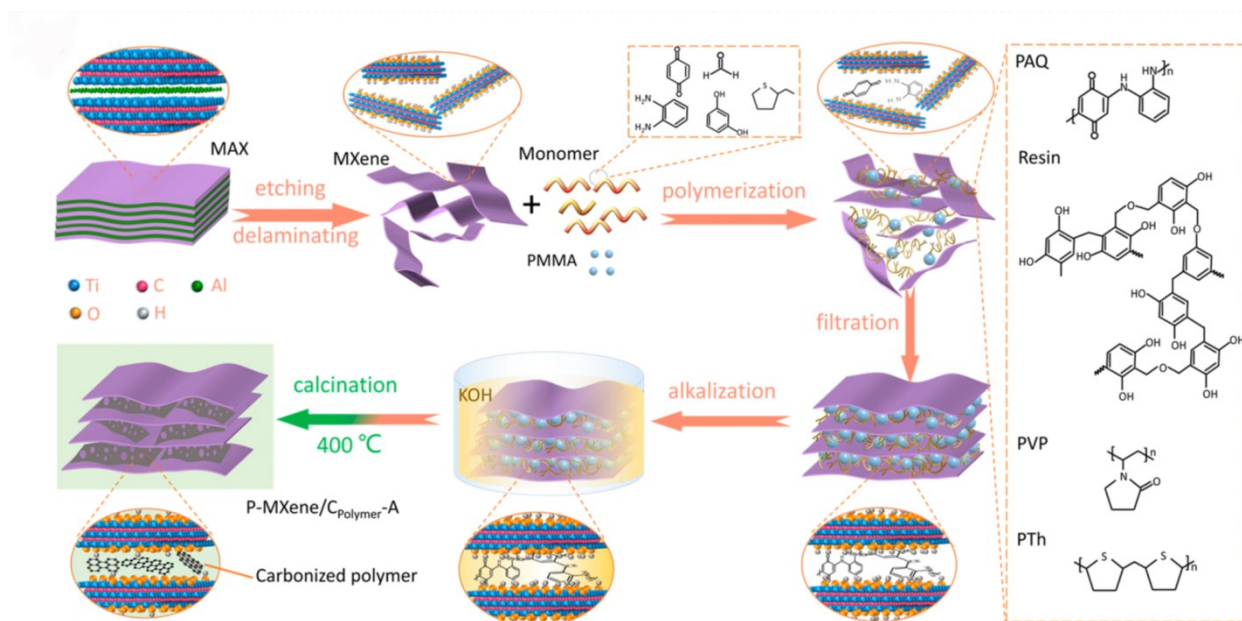


Figure 1: Schematic diagram showing the basic preparation process of P-MXene/ C_{PAQ} -A thin film electrode; Adapted from: “Self-Supporting, Binder-Free, and Flexible $Ti_3C_2T_x$ MXene-Based Supercapacitor Electrode with Improved Electrochemical Performance| ACS Nano.” Accessed: Nov. 14, 2024. Available: <https://pubs.acs.org/doi/10.1021/acsnano.2c03351>

2.3. Preparation of NP-MnO₂ electrode

The NP-MnO₂ electrode was prepared following the method reported by Mahmoud et al[29]. with slight modifications. The porous manganese dioxide (Mn O₂) was synthesized through an electrochemical deposition technique, utilizing a standard three-electrode system to ensure precise deposition. The electrolyte solution used for this process comprised 0.25 M manganese acetate tetrahydrate ((CH₃COO)₂Mn·4H₂O), specifically prepared for plating. A potentiostatic method was employed during the deposition, maintaining a constant potential of 1 V at room temperature (25 °C). The target of the deposition was a freshly cleaned stainless steel current collector, providing a working electrode surface of 2 cm² for each face of the sample [29].

Following the deposition, the MnO₂ film on the stainless steel was gently rinsed with distilled water to remove any residual electrolyte and then left to air dry at ambient temperature (25 °C). The final mass loading of the MnO₂ films was finely controlled to achieve a density of 0.1 mg per cm²[29]

2.4. Assemble ACS

The device configuration was carefully designed for optimal performance to assemble the asymmetric supercapacitor (ASC) device using nanoporous manganese dioxide (NP-MnO₂) as the positive electrode. The negative electrode was constructed from the P-MXene/C_{PAQ}-A material, which brings exceptional electrical conductivity and capacitive properties. In contrast, the positive electrode utilized the NP-MnO₂, known for its high pseudocapacitive behavior and porous structure that enhances ion diffusion.

The two electrodes were separated by a Celgard 3501-coated polypropylene membrane, which acts as a physical barrier to prevent electrical contact while allowing ionic transport through its porous structure. The entire assembly was saturated with a 3 M sulfuric acid (H₂SO₄) aqueous solution serving as the electrolyte. This choice of electrolyte was due to its ability to provide high ionic conductivity and chemical stability within the operating voltage window of the supercapacitor.

For the current collectors, glassy carbon was used to ensure that the electrical currents were efficiently conducted from the electrodes to the external circuit. Glassy carbon is favored in such configurations for its chemical inertness and superior conductivity. This setup aimed to leverage the distinct advantages of both electrode materials—combining the high surface area and pseudo capacitance of NP-MnO₂ with the conductive and flexible nature of P-MXene/C_{PAQ}-A—to produce a supercapacitor device that exhibits a balanced energy and power density suitable for advanced energy storage applications.

2.5. Materials analysis method

NMR (Nuclear Magnetic Resonance Spectroscopy) is used to calculate the element types and components of the electrode. The samples were dried in a vacuum oven overnight cut 3.5 mg of the sample was cut in a 2 ml small bottle, then, dissolved in 0.7 ml cheliform-d and transferred to the NMR tube. After the NMR analysis, Top Spine was used to measure the peak peaks and the area of the peaks. After the elements are up to the standard the next step is to use SEM (Scanning elemental microscopy) to determine the electrode topographical surface and the elemental composition. TEM (Transmission electron microscopy) is used to study its shape and size. The samples were using ultrasonic treatment to make the sample dissolve in the deionized water. Then, drop the nano-reagent on 200 mesh copper grids and wait for the drying of the solvent. After analyzing the electrode with SEM and TEM, the next step involves using X-ray Diffraction (XRD) to investigate the crystallographic structure of the electrode material. XRD will help identify the phases present and provide information on the crystal structure, lattice parameters, and crystallite size. The sample should be finely ground, and a thin layer can be placed on a glass slide for analysis. X-ray Photoelectron Spectroscopy (XPS) will also be employed to analyze the elemental composition, chemical states, and electronic state of the elements within the electrode material. XPS is particularly useful for understanding the surface chemistry and any changes that might have occurred during the electrode's synthesis or processing. For this, the sample will be prepared by mounting it onto an XPS sample holder, ensuring that the surface is clean and free from contaminants.

These roughness parameters provide quantitative insights into the electrode's surface texture, which can be correlated with the morphological observations from SEM and TEM. SEM images can validate how the surface topography (including nanoscale pores or protrusions), while TEM can confirm nanoparticle distribution and agglomeration that may affect the values.

Table 1: Changes of roughness parameters of NP-MnO₂; Data from: “Enhanced energy storage for nano-structural porous MnO₂//AC/MWCNTs asymmetric hybrid supercapacitor device in Na₂SO₄ aqueous electrolyte | Journal of Materials Science: Materials in Electronics.” Accessed: Nov. 14, 2024. Available: <https://link.springer.com/article/10.1007/s10854-021-07156-y>

Composition	Roughness average (R_a): (nm)	Average maximum height of the roughness (R_{tm}): (nm)	Average maximum roughness valley depth (R_{vm}): (nm)	Average maximum roughness peak height (R_{pm}): (nm)	Skewness (R_{sk}):	Kurtosis (R_{ku}):
NP-MnO ₂	11.1	86.7	44.2	42.4	-0.00025	3.2

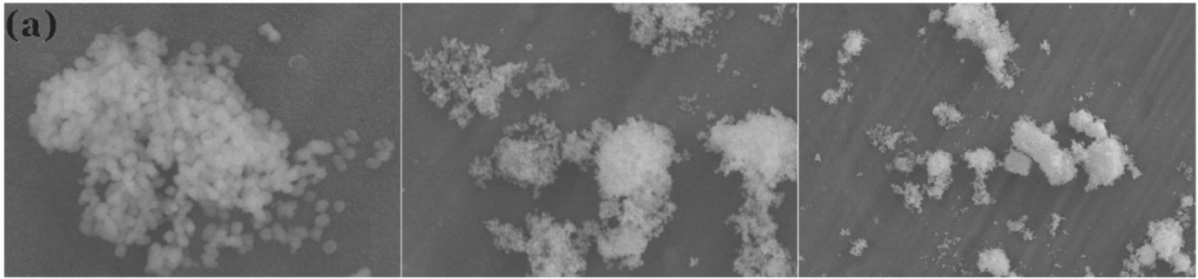


Figure 2: a) SEM morphology of NP-MnO₂ at different magnifications; Adapted from: “Enhanced energy storage for nano-structural porous MnO₂//AC/MWCNTs asymmetric hybrid supercapacitor device in Na₂SO₄ aqueous electrolyte | Journal of Materials Science: Materials in Electronics.” Accessed: Nov. 14, 2024. Available: <https://link.springer.com/article/10.1007/s10854-021-07156-y>

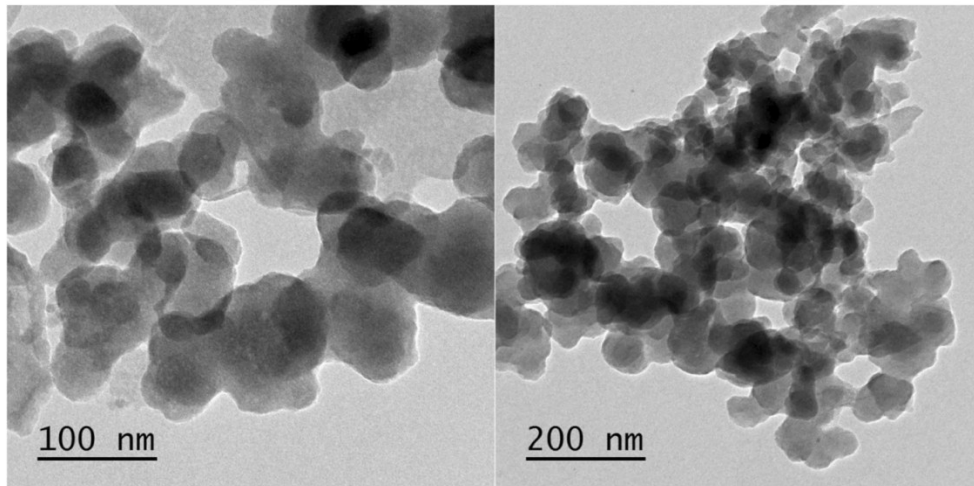


Figure 3: TEM of NP-MnO₂; Adapted from: “Enhanced energy storage for nano-structural porous MnO₂//AC/MWCNTs asymmetric hybrid supercapacitor device in Na₂SO₄ aqueous electrolyte | Journal of Materials Science: Materials in Electronics.” Accessed: Nov. 14, 2024. Available: <https://link.springer.com/article/10.1007/s10854-021-07156-y>

2.6. Electrochemical characterizations

In the study of the latest developed asymmetric supercapacitors (ACS) featuring NP-MnO₂ and P-MXene/C_{PAQ}-A electrodes, a comprehensive electrochemical analysis is conducted using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), all within a three-electrode setup. The CV tests are designed to assess the electrochemical behavior of the electrodes across a wide potential range, typically up to 1.9 V for these ACS configurations. The tests are performed at varying scan rates, from 10 to 100 mV/s, using NP-MnO₂ or P-MXene/C_{PAQ}-A as the working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. This setup allows for precise measurement of the capacitive behavior and the material's response to different charging rates, offering insights into the energy storage capabilities of the electrodes.[28], [29]

The GCD technique complements the CV by providing data on the charge-discharge efficiency and the stability of the electrodes over time. In this method, the electrodes are subjected to a constant current while monitoring the potential changes, with tests conducted over the full voltage range (up to 1.9 V) and at various current densities (e.g., 0.5 to 10 A/g). The same three-electrode setup is used, with NP-MnO₂ or P-MXene/C_{PAQ}-A as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference. The results from GCD tests reveal the specific capacitance, energy density, power density, and cycle life of the supercapacitors, which is crucial for evaluating their performance in practical applications.[28], [29]

Additionally, EIS is employed to investigate the frequency response of the supercapacitors, providing a deeper understanding of the resistive and capacitive properties of the electrode materials. EIS measurements, conducted within the same three-electrode configuration, yield Nyquist plots that detail the charge transfer resistance (R_{ct}) and equivalent series resistance (ESR), key parameters that influence the overall efficiency and effectiveness of the supercapacitor.

3. Conclusion

Supercapacitor technologies are incorporating novel features that significantly enhance their functionality and broaden their applications, gradually beyond traditional energy storage. Firstly, the development of flexible and wearable supercapacitors is enabling integration into wearable electronics and smart textiles[29]. This is achieved through materials like carbon-based materials, metal oxides, and conducting polymers that maintain performance under mechanical deformation[29]. Moreover, the advent of transparent supercapacitors allows them to be embedded into displays and windows without obstructing visibility, utilizing ultra-thin conductive materials such as carbon-based transparent conductive electrodes (TCEs), conductive polymer-based TCEs, metal-based TCEs, and hybrid -based TCEs[28], [29], [34]. In addition, the introduction of impact-resistant supercapacitors using hydrogel-infused lattice structures enhances their mechanical durability. These innovative designs incorporate hydrogels within lattice frameworks, providing excellent energy absorption capabilities that protect the supercapacitor from mechanical shocks and impacts, thereby improving their resilience in demanding environments[35]. Furthermore, incorporating self-healing properties using polymers that autonomously repair mechanical damage enhances the durability and lifespan of supercapacitors[36], [37], [38]. Additionally, the miniaturization of supercapacitors into micro and nanoscale devices enables on-chip energy storage for microelectronics, which is crucial for the advancement of miniaturized devices[39], [40], [41]. Lastly, innovations in advanced manufacturing techniques, such as 3D printing, facilitate the customization of supercapacitor shapes and architectures to fit specific applications, broadening their potential uses in various industries[42], [43], [44]. Together, these novel features are revolutionizing the design and application of supercapacitors, making them more versatile and adaptable to the demands of modern technology.

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