Binary transition metal oxides vs. Binary metal oxides for electrochemical Supercapacitors: Performance, Challenges, and Future Prospects

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Abstract

This review investigates the potential of molybdate nanocomposites with the general formula ABO_4 (A = Mg, Ca, Sr, or Ba; and B = Mo) as advanced electrode materials for aqueous energy storage systems. Electrochemical energy storage technologies, such as supercapacitors and batteries, offer distinct advantages over mechanical and thermal systems, including higher energy efficiency, faster response times, modular scalability, and integration with renewable energy sources.

Among the various electrochemical energy storage technologies, supercapacitors are distinguished by their high-power density, rapid charge–discharge rates, and long cycle life, positioning them as strong candidates for next-generation applications. Binary transition metal oxides (BTMOs) such as cobaltates, ferrates, manganates, vanadates, and molybdates have been extensively studied due to their superior electrochemical performance, owing to their multiple redox states, structural stability, and high electrical conductivity, largely attributed to the synergistic interactions between transition metal ions. In comparison, binary metal oxides (BMOs) with the general formula $MMoO_4$ (M = Mg, Ca, Sr, or Ba) represent a distinct class of oxides with distinguishing crystallographic features. Their crystal structures are influenced by the ionic radius of the divalent cation: wolframite-type structures form when A = Mg (< 0.99

Å), while scheelite-type structures are observed for Ca, Sr, and Ba (> 0.99 Å). Specifically, $MgMoO_4$ typically adopts the wolframite structure, characterized by octahedral coordination of Mo, whereas $CaMoO_4$, $SrMoO_4$, and $BaMoO_4$ generally crystallise in the scheelite structure, where Mo is tetrahedrally coordinated. Despite their structural versatility and inherent stability, BMOs with ABO_4-type composition remain underexplored compared to BTMOs. However, their tunable crystal chemistry and the combined properties of alkaline-earth and transition-metal elements make them promising materials for advanced supercapacitor electrode materials.

This review summarises recent progress in doping and hybridization strategies aimed at enhancing the electrochemical performance of $BaMoO_4$ and related molybdate-based materials. Doping can effectively alter charge carrier concentrations and tailor electronic properties, thereby improving energy storage capabilities. Although doping can significantly enhance charge transport and electrochemical activity, the synthesis of well-defined molybdate nanostructures remains a major challenge, limiting their scalability and practical deployment. A promising approach involves the hybridization of $BaMoO_4$ with ZnO, a semiconductor renowned for its excellent electrical conductivity and mechanical robustness. Combustion synthesis of $BaMoO_4$/ZnO nanocomposites has yielded materials with improved energy and power densities, demonstrating synergistic effects between the two components. These advancements underscore the growing potential of $BaMoO_4$/ZnO-based systems in the development of sustainable and high-performance energy storage technologies.

Keywords: ABO_4 molybdates; binary; transition; supercapacitors; scheelite.

Contents

1. INTRODUCTION

The growing global demand for energy and environmental concerns over fossil fuel reliance have accelerated the shift toward renewable energy sources [1]. However, the intermittent nature of solar and wind power continues to challenge grid reliability, reinforcing the importance of developing robust and efficient Energy Storage Systems (ESS) [2]. Among various ESS technologies, supercapacitors stand out for their high power density, fast charge-discharge rates, and long cycle life, with performance largely dictated by the design and properties of their electrode materials [3]. In this context, Binary Transition Metal Oxides (BTMOs) and Binary Metal Oxides (BMOs) have attracted increasing attention due to their contrasting but complementary features, where BTMOs offer high pseudocapacitance and multiple redox-active sites, while BMOs provide structural robustness and long-term stability. Understanding and comparing these two oxide families is therefore essential for advancing high-performance supercapacitor electrodes.

Recent advances in nanomaterials have opened new avenues for enhancing supercapacitor performance through the development of cost-effective and sustainable electrode composites. A particularly promising strategy involves the integration of alkaline-earth and semiconductors, forming hybrid nanostructures that simultaneously optimize energy and power densities [4]. Within this context, two oxide families have emerged as key contributors they are (a) binary transition-metal oxides (BTMOs) containing two different transition metal cations such as, including $NiMoO_4$, $CoMoO_4$, $MnMoO_4$, $NiFe_2O_4$, and $Ni_3V_2O_8$, and (b) binary metal oxides (BMOs) of the ABO_4 type (where A = Mg, Ca, Sr, Ba; and B = Mo).

BTMOs are well-established for their high pseudocapacitance, attributed to multiple redox couples (e.g., Ni^{2+}/Ni^{3+}, Co^{2+}/Co^{3+}, Mn^{3+}/Mn^{4+}) that facilitate fast, surface-confined faradaic reactions. Nanostructuring these materials into sheets, rods, or mesoporous frameworks routinely elevates their specific capacitance to values exceeding 450 F g^{-1}. For instance, well-dispersed $NiFe_2O_4$ nanorods on graphene sheets [5] have demonstrated a specific capacitance of ~483 F g^{-1} at 0.1 A g^{-1}, and 298 F g^{-1} at 10 A g^{-1}accompanied by excellent cycling stability over 10,000 without obvious capacitance attenuation. Further enhancements are achieved through coupling with graphene oxide. $NiFe_2O_4$/graphene composites improve electron/ion transport and mitigate restacking. The defect engineering in the composites, such as oxygen vacancies or heteroatom doping, accelerates charge transfer and enhances durability. To maintain these gains at practical electrode loadings, engineered porosity and low internal resistance are essential for achieving strong areal and volumetric performance.

In parallel, ABO_4 type BMOs, including scheelite-type $CaMoO_4$, $SrMoO_4$, and $BaMoO_4$, as well as wolframite-type $MgMoO_4$, are gaining attention for their structural robustness and chemical stability. The alkaline earth molybdates are wide gap semiconductors, and they are supposed to exhibit electrochemical properties. Although their intrinsic conductivity is generally lower than that of BTMOs, the presence of Mo cations introduces additional redox activity and broadens electrolyte compatibility. Recent strategies, such as carbon scaffolding with graphene or carbon nanotubes (CNTs), aliovalent doping, and morphology control, have significantly improved their electrochemical response [6]. These materials are particularly effective in hybrid supercapacitors, where pairing with capacitive carbons expands the operating voltage window and enhances energy density without compromising power performance.

The contrasting electrochemical behavior of BTMOs and BMOs can be attributed to their distinct structure–property relationships. BTMOs exhibit rich redox activity near the Fermi level, enabling high pseudocapacitance, while BMOs offer more stable but less conductive frameworks that benefit from structural enhancement. Layered or spinel structures in BTMOs facilitate ion transport and redox kinetics, whereas scheelite-type molybdates provide rigid lattices conducive to long-term cycling stability [7-8]. Morphology and porosity are also critical, as nanostructuring increases active surface area and reduces ion diffusion lengths, although excessive microporosity may hinder access for solvated ions. At the device level, optimized mass loading and conductive percolation networks are essential to translate high gravimetric capacitance into meaningful areal and volumetric performance.

Representative examples, such as $NiMoO_4$ nanosheets on conductive foams and $BaMoO_4$–graphene composites, illustrate the benefits of integrating crystal chemistry, morphology engineering, and hybridization. These design strategies not only enhance intrinsic redox activity but also ensure stability under practical cycling conditions [8]. Among BMOs, barium molybdate ($BaMoO_4$), a compound combining an alkaline-earth metal with a transition metal, has emerged as particularly promising due to its robust structure, electrochemical activity, and redox versatility. When hybridized with zinc oxide (ZnO), a wide-bandgap semiconductor known for its stability and ease of synthesis, $BaMoO_4$/ZnO nanocomposites exhibit synergistic effects, including enhanced battery discharge capacity [9], improved cycling durability, and superior charge-transfer efficiency compared to pristine $BaMoO_4$.

This review critically examines the roles of BTMOs and BMOs as supercapacitor electrode materials, with emphasis on structural and morphological factors, synthesis and processing strategies, and device-level performance metrics. It also explores the emerging role of BMOs in hybrid configurations and concludes with perspectives on the challenges and future opportunities for scalable, high-performance energy storage systems. Finally, while the focus remains on the fundamental properties of BTMOs and BMOs, it is essential to situate these materials within the broader energy landscape. Supercapacitors, increasingly considered alongside batteries and fuel cells, play a pivotal role in hybrid energy storage systems for renewable integration, grid stabilization, and electric mobility. Continued innovation in electrode materials is therefore critical to advancing sustainable energy technologies.

2. ENERGY - GLOBAL SCENARIO

Energy is the foundation of modern civilization, driving economic growth, technological innovation, and societal well-being [10]. It powers industries, transportation, agriculture, and homes, while also enabling critical services such as healthcare, education, and communication. Despite these benefits, fossil fuels still account for 81% of the global total energy supply (TES), as illustrated in **Figure 1**, with oil making up nearly 30%, followed by coal (28%) and natural gas (23%). This heavy reliance on fossil fuels has led to serious environmental consequences, including climate change, air pollution, and biodiversity loss, highlighting the urgent need for a transition to more sustainable energy sources. [11]

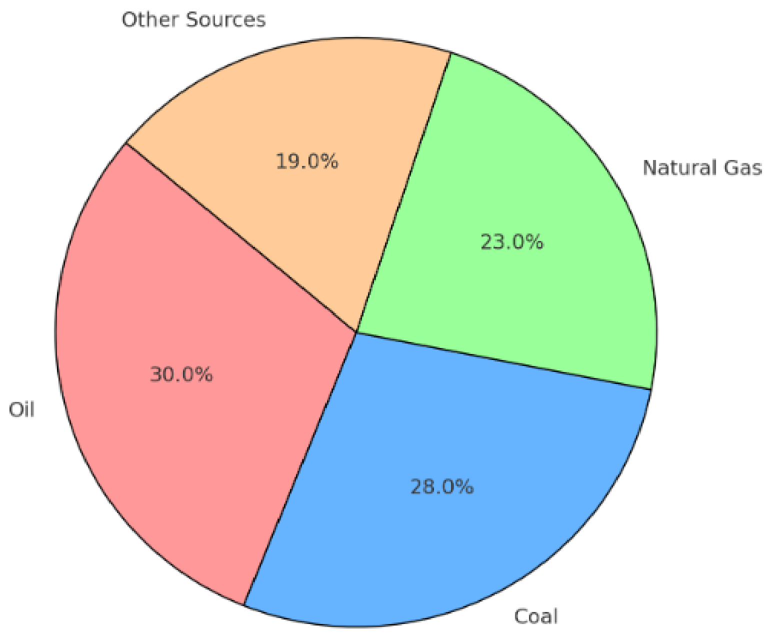

Figure 1 *Total Energy Supply (TES) Globally in 2023, data extracted from [11].*

Since the Industrial Revolution, the global energy system has undergone a profound transformation. Today, energy demand continues to rise across many countries, driven by growing populations and increasing wealth. This surge in consumption underscores the urgent need to transition from fossil fuels to low-carbon energy sources—not only to meet future demand but also to reduce our reliance on carbon-intensive fuels. Global energy use is increasing at an average rate of 1% to 2% per year [12]. The chart in **Figure 2** illustrates global primary energy consumption by source, highlighting the continued dominance of fossil fuels in the global energy mix.

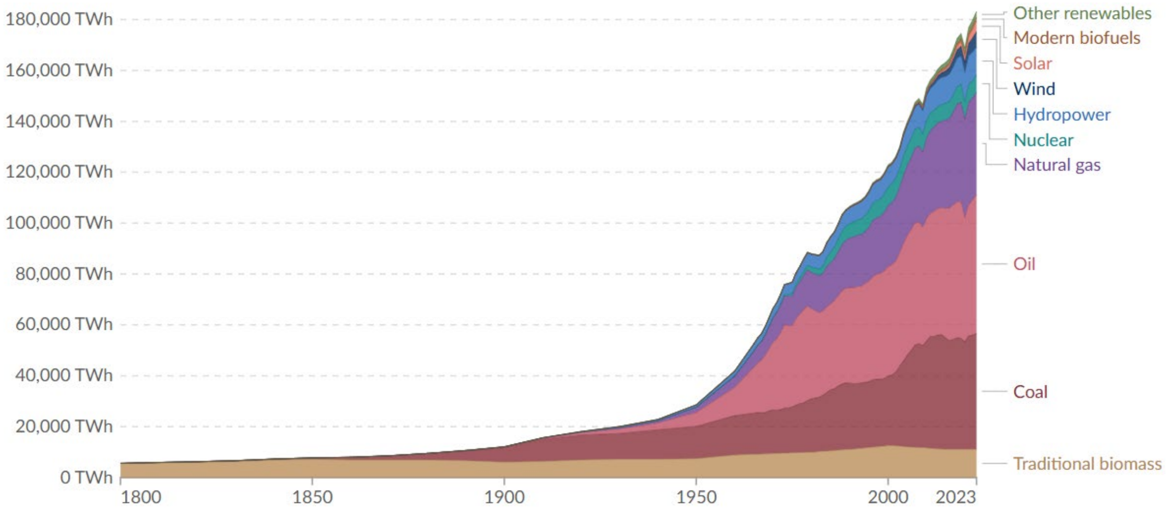

Figure 2 Global Primary Energy Consumption by source in terawatt-hours [12]. Reproduced under the terms of the Creative Commons CC BY license.[12] Copyright 2023, The Author(s).

3. RENEWABLE ENERGY - ROLE IN THE GLOBAL ENERGY TRANSITION

Thus, Renewable Energy (RE), derived from naturally replenished processes such as solar, wind, hydro, and geothermal sources, offers a sustainable and environmentally responsible alternative to fossil fuels. These energy sources are essential for reducing greenhouse gas emissions, mitigating climate change, and enhancing energy security through the diversification of energy supply [13]. Moreover, the renewable energy sector contributes significantly to economic development, generating employment opportunities in manufacturing, installation, and maintenance. In 2022 alone, the sector employed approximately 13.7 million people worldwide [14]. The RE sector is currently undergoing rapid expansion. By the end of 2022, global renewable energy capacity had reached 3,372 gigawatts (GW), with solar and wind power comprising the majority of new installations [15].

Looking ahead, renewable energy is expected to play a central role in the global energy transition. In a net-zero emissions scenario, as evidenced in **Figure 3**, it is projected to supply nearly 90% of global electricity by 2050 [16]. This transformation will be driven by technological advancements in energy storage and grid integration, supportive policy frameworks, and the increasing cost competitiveness of renewable technologies. [16]. In addition to environmental and economic benefits, renewable energy enhances energy security by reducing reliance on imported fossil fuels and mitigating the geopolitical risks associated with their supply chains [17]. Furthermore, renewables are poised to decarbonize hard-to-abate sectors, such as transportation and heavy industry, through electrification and the deployment of green hydrogen technologies [17].

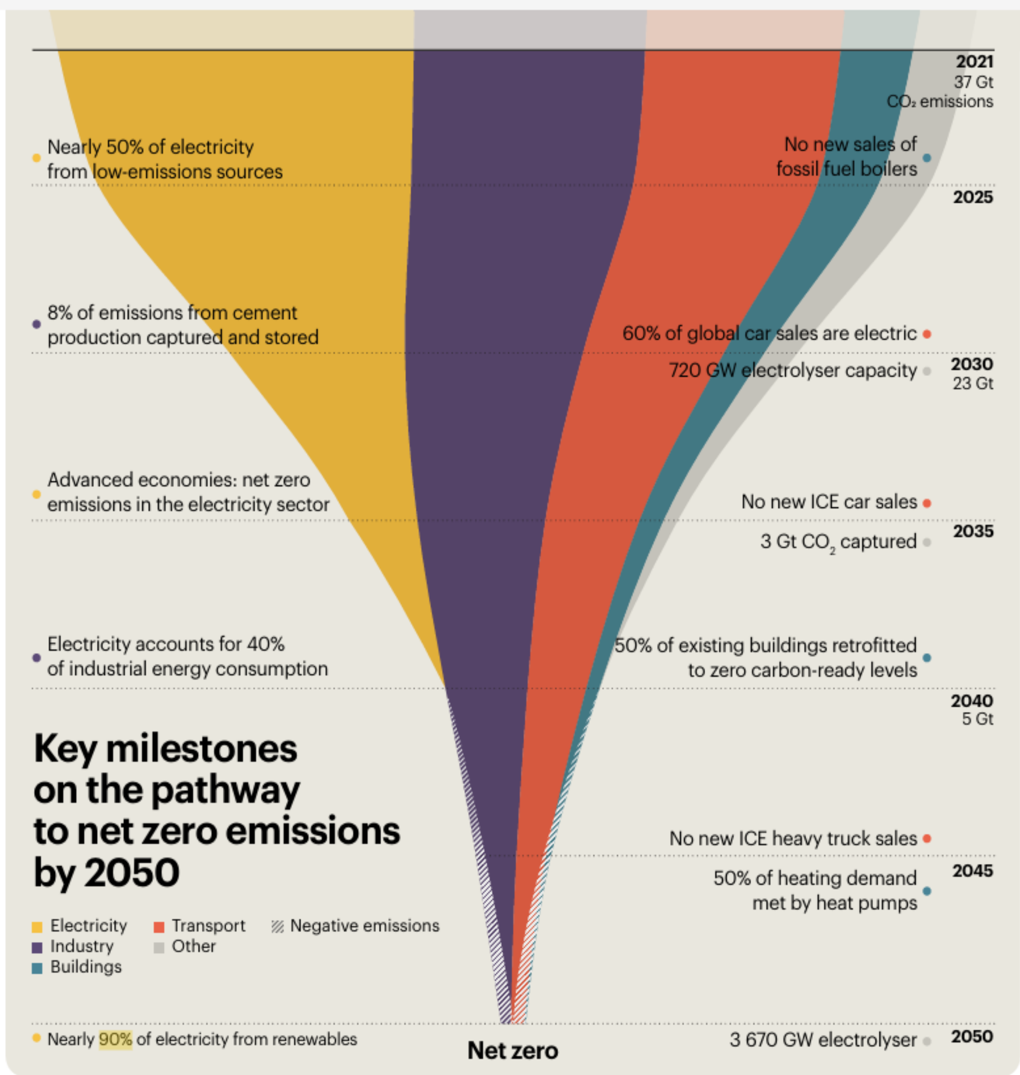

Figure 3 *RE Share by 2050 [16]*

Despite these advantages, integrating high shares of renewable energy into power grids presents several challenges due to their inherent intermittency and variability [18]. These challenges include:

(a) reduced grid reliability and security,

(b) significant renewable energy curtailment, which undermines cost-effectiveness, and

(c) increased demand for system flexibility and reserve capacity to balance supply and demand.

To address these issues, a range of energy storage technologies is emerging as a promising solution, enabling the integration of larger shares of renewables into future energy systems [18].

4. ENERGY STORAGE SYSTEMS (ESS)

An energy storage system (ESS) is a technology designed to capture energy produced at one time for use at a later time. It plays a pivotal role in balancing energy supply and demand, facilitating the integration of renewable energy (RE) sources, and enhancing grid stability [19]. ESS is particularly vital in addressing the intermittency and variability of renewable sources such as solar and wind, which do not produce power consistently. As the deployment of these intermittent sources increases, the demand for robust energy storage solutions becomes more pressing. Moreover, ESS contributes to reducing reliance on fossil fuels, mitigating geopolitical risks linked to energy imports, and strengthening resilience against energy supply disruptions [20]. Consequently, ESS has emerged as a cornerstone technology for achieving higher shares of renewables in the energy mix and advancing global climate objectives [21]. Various ESS technologies, such as batteries, pumped hydro storage, flywheels, thermal storage, and supercapacitors, offer distinct characteristics tailored to specific applications [22]. The following diagram (Figure 4) illustrates the range of energy storage technologies currently in use.

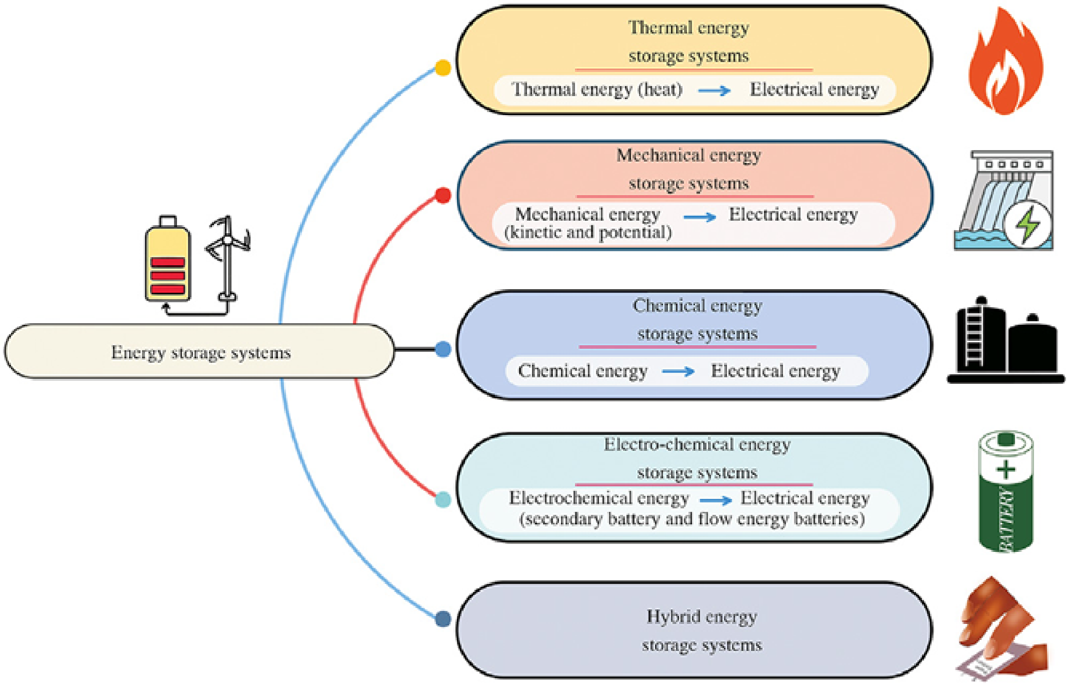

Figure 4 Classification of Energy Storage Technologies [23]. Reproduced with permission from ref 23. Copyright 2022, Elsevier Ltd.

4.1 Thermal Energy Storage (TES)

Thermal Energy Storage (TES) is a technology that captures and stores thermal energy by heating or cooling a storage medium, enabling the energy to be used later for heating, cooling, or power generation. TES systems help balance energy supply and demand, enhance energy efficiency, and reduce peak loads on energy infrastructure. There are three primary types of TES, as shown in Figure 5, and the mechanisms [24] :

i. **Sensible Heat Storage (SHS):** Stores energy by raising or lowering the temperature of a solid or liquid medium, such as water, molten salts, or rocks

ii. **Latent Heat Storage (LHS)**: Stores energy during a material's phase change (e.g., from solid to liquid), using substances like paraffin wax or salt hydrates.

iii. **Thermochemical Storage (TCS)**: Stores energy through reversible chemical reactions that absorb or release heat.

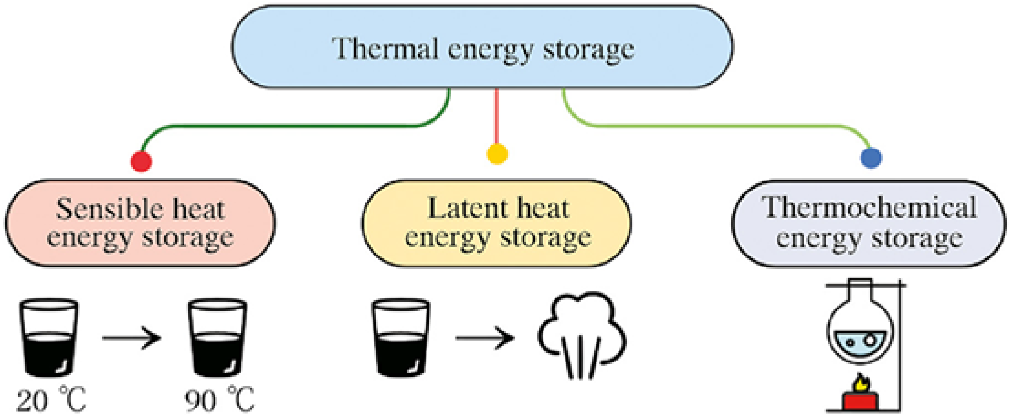

Figure 5 Three primary types of TES [23]. Reproduced with permission from ref 23. Copyright 2022, Elsevier Ltd.

4.2 Mechanical Energy Storage (MES)

Mechanical Energy Storage (MES) systems store energy in the form of mechanical potential or kinetic energy. This energy can be converted into mechanical work and subsequently transformed back into electrical energy when needed. There are four primary types of MES systems, as shown in Figure 6, and they are [25-26]:

i. Pumped Hydro Storage (PHS): Energy is stored by pumping water from a lower reservoir to a higher one. When electricity is needed, the water is released back down through turbines to generate power.

ii. Compressed Air Energy Storage (CAES): This system stores energy by compressing air and storing it in underground caverns or tanks. When required, the compressed air is released to drive turbines and produce electricity.

iii. Flywheel Energy Storage (FES): Energy is stored as rotational kinetic energy in a spinning rotor. The stored energy is released by slowing down the rotor, converting its motion back into electricity.

iv. Gravitational Energy Storage System (GES). As an alternative to PHS, which faces limitations due to geography and water availability, GES systems use gravity to store energy. These systems lift a heavy mass, such as a piston, using water or mechanical means. When energy is needed, the mass is lowered, causing water to flow through hydroelectric generators and produce electricity [23].

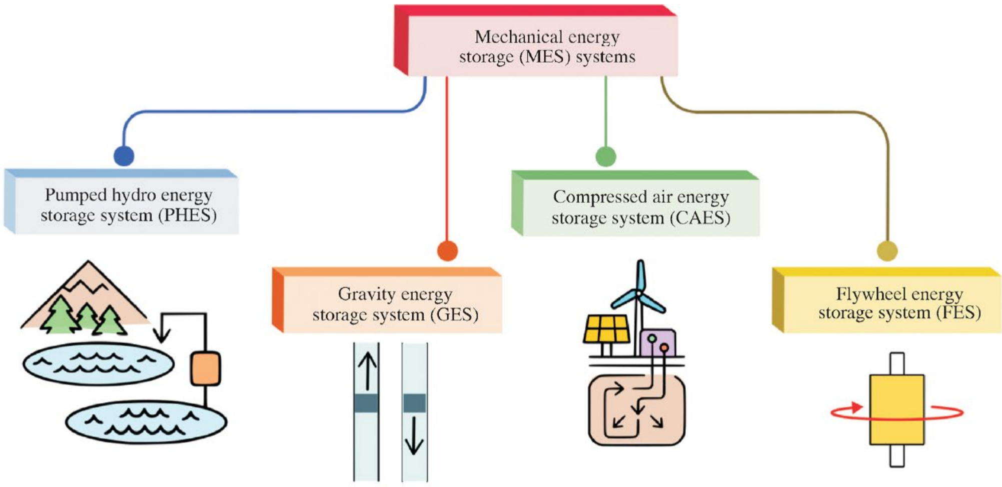

Figure 6 Four primary types of MES [23]. Reproduced with permission from ref 24. Copyright 2022, Elsevier Ltd.

4.3 Chemical Energy Storage (CES)

Chemical Energy Storage (CES) systems store energy in the form of chemical bonds, which can be released through chemical reactions. This energy is typically contained within fuels or other chemical compounds (shown in Figure 7) and can be converted into usable forms, such as heat or electricity, when required. While renewable resources used in hydrogen production are abundantly available, their intermittent and variable nature poses a significant challenge to the widespread adoption of a hydrogen-based economy. The primary types of CES systems include [23]:

i. Hydrogen Storage: Energy is stored as hydrogen gas, which can be utilized in fuel cells or combustion engines to generate electricity or mechanical power.

ii. Synthetic Fuels: Energy is stored in synthetic hydrocarbons, such as methane, methanol, or ammonia, produced through processes like electrolysis and Fischer-Tropsch synthesis

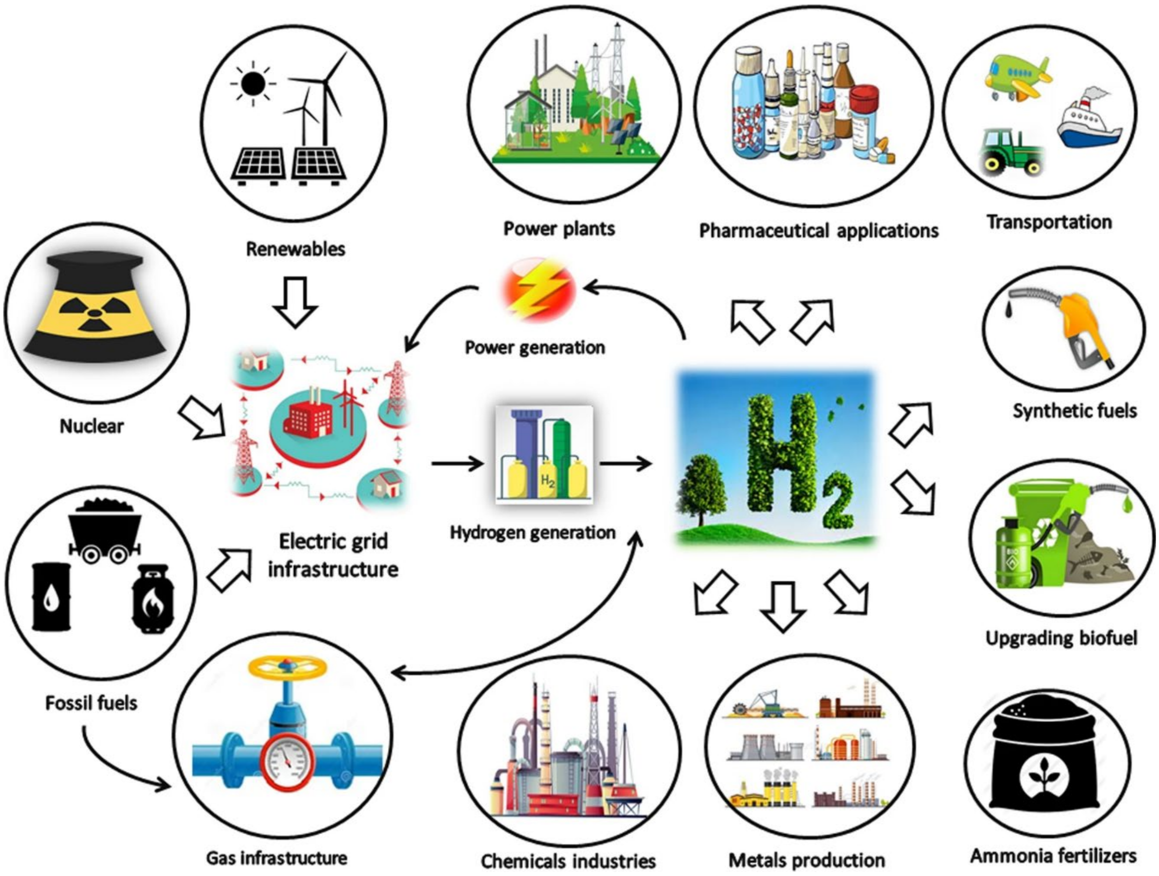

Figure 7 Hydrogen production routes, including renewables, fossil fuels, and nuclear, with hydrogen being produced in power plants, and being stored for various applications. Reproduced under the terms of the Creative Commons CC BY 4.0 license [25] Copyright 2022, The Author(s).

4.4 Electrochemical Energy Storage (EES)

Electrochemical Energy Storage (EES) systems store energy in chemical form and convert it into electrical energy through electrochemical reactions. The most common types of EES systems include batteries, supercapacitors, and fuel cells [26]. The charge storage mechanisms for these systems are illustrated in Figure 8.

i. Batteries: These store energy in electrochemical cells composed of an anode, a cathode, and an electrolyte. Common examples include lithium-ion batteries, lead-acid batteries, and solid-state batteries.

ii. Supercapacitors: These store energy via electrostatic charge separation at the electrode–electrolyte interface, enabling rapid charging and discharging cycles.

iii. Fuel Cells: These convert chemical energy from fuels (such as hydrogen) into electricity through electrochemical reactions with an oxidizing agent, typically oxygen.

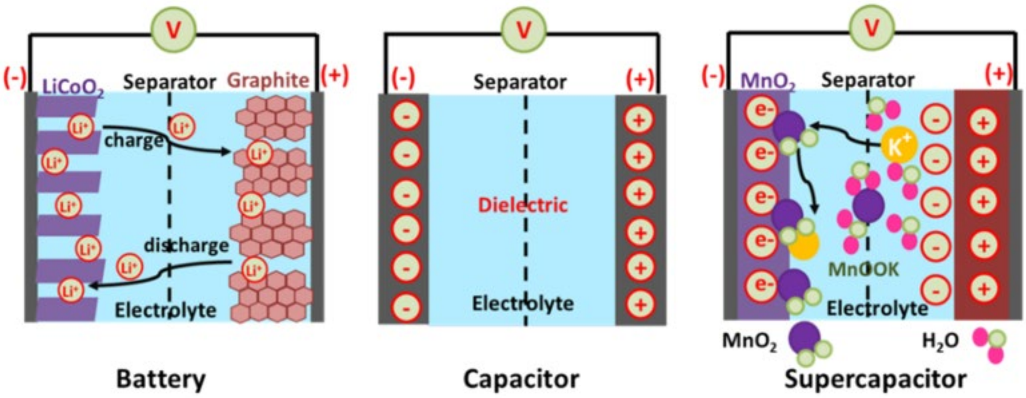

Figure 8 Charge storage mechanisms in battery, capacitor, and supercapacitor [27].

4.5 Hybrid Energy Storage (HES) System

The Hybrid Energy Storage (HES) system concept integrates the strengths of various Energy Storage Systems (ESSs) to achieve optimal performance. ESSs are generally categorized into two types: high-power density systems and high-energy density systems. High-power density systems, such as supercapacitors and flywheels, are designed for rapid energy delivery over short durations. These systems respond within milliseconds or seconds, making them ideal for applications requiring quick bursts of power, such as frequency regulation, regenerative braking in electric vehicles, or power smoothing. However, their energy storage capacity is limited, which restricts their use to short-term operations [23].

In contrast, high-energy density systems, including lithium-ion batteries, flow batteries, and hydrogen storage, are capable of storing and delivering energy over extended periods. Although they typically have slower response times, they are well-suited for applications like load shifting, backup power, and renewable energy time-shifting. These systems can handle larger energy demands but may face challenges such as limited power output and degradation under high current loads.[23].

5. PERFORMANCE OF DIFFERENT ENERGY STORAGE SYSTEMS

Energy Storage Systems (ESS) are utilized for specific tasks depending on their performance characteristics and suitability for particular applications. One widely used method for evaluating and comparing ESS technologies is the Ragone plot, which illustrates the relationship between specific energy (energy per unit mass, typically in Wh/kg) and specific power (power per unit mass, typically in W/kg). This plot effectively visualizes the trade-offs between how much energy a device can store and how quickly it can deliver that energy [28]. As shown in the Ragone plot (Figure 9), supercapacitors occupy the intermediate space between batteries (which offer high energy density) and conventional capacitors (which provide high power density). This positioning makes supercapacitors particularly suitable for applications requiring a balance of high-power output and short-duration energy delivery. Consequently, they are favored in scenarios where power, speed, and longevity are more critical than total energy storage capacity [27].

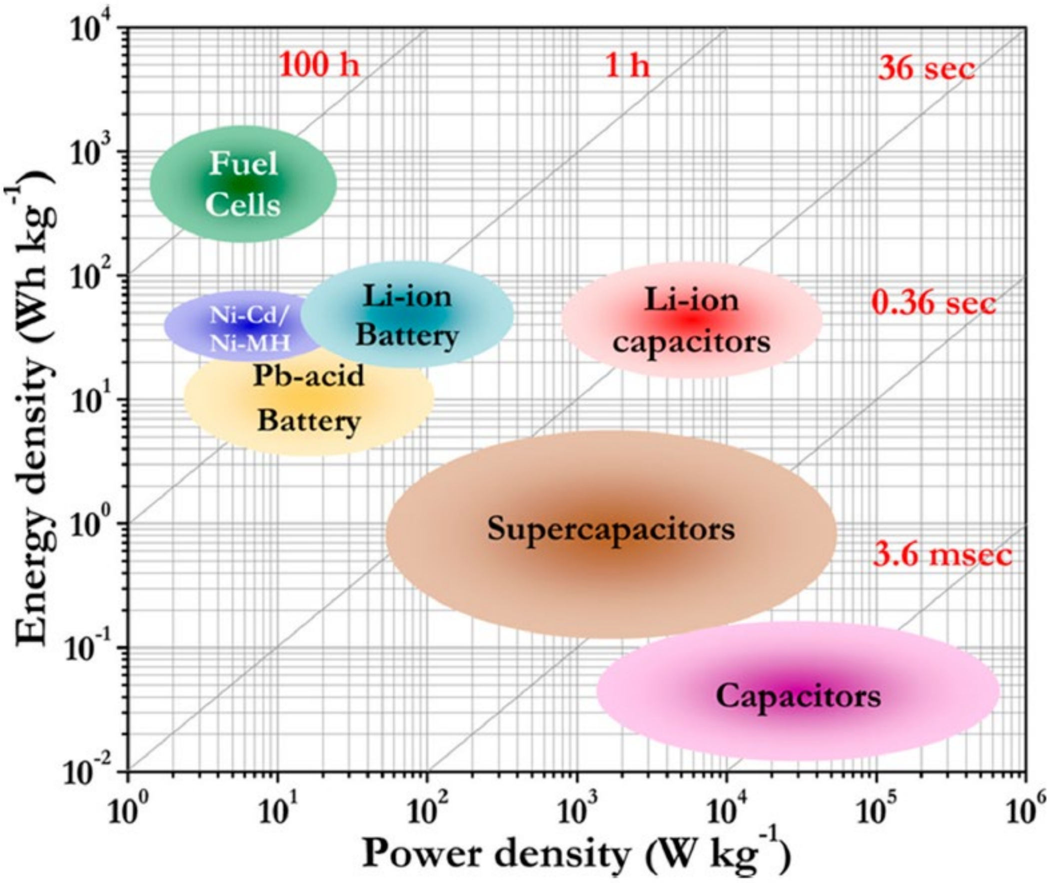

Figure 9 Ragone Plot for different Energy Storage Devices [28].

Figure 10 presents a radar chart comparing various ESS technologies, such as batteries, supercapacitors, flywheels, and fuel cells, across key performance metrics. Batteries are noted for their good energy density and cost-effectiveness per kWh, but are limited by lower cycle life. Flywheels excel in operating temperature range and power density, while fuel cells lead in cell voltage and charge retention. Supercapacitors stand out in terms of cyclability, power density, safety, and cost-effectiveness per kW, making them ideal for high-power, rapid-cycling applications, despite their limitations in energy density and cell voltage. Each technology presents distinct trade-offs, underscoring the importance of aligning energy storage solutions with specific application requirements [29]. The primary objective of this article is to critically compare Binary Transition Metal Oxides (BTMOs) and Binary Metal Oxides (BMOs) as electrode materials for electrochemical energy storage, with a particular emphasis on their application in supercapacitor electrodes. This comparative analysis explores their electrochemical performance, structural and compositional challenges, and prospects for scalable energy storage systems. To fully assess their potential, it is essential to examine both the performance characteristics and the underlying mechanisms that govern their operation. These aspects are systematically reviewed and discussed in the following sections.

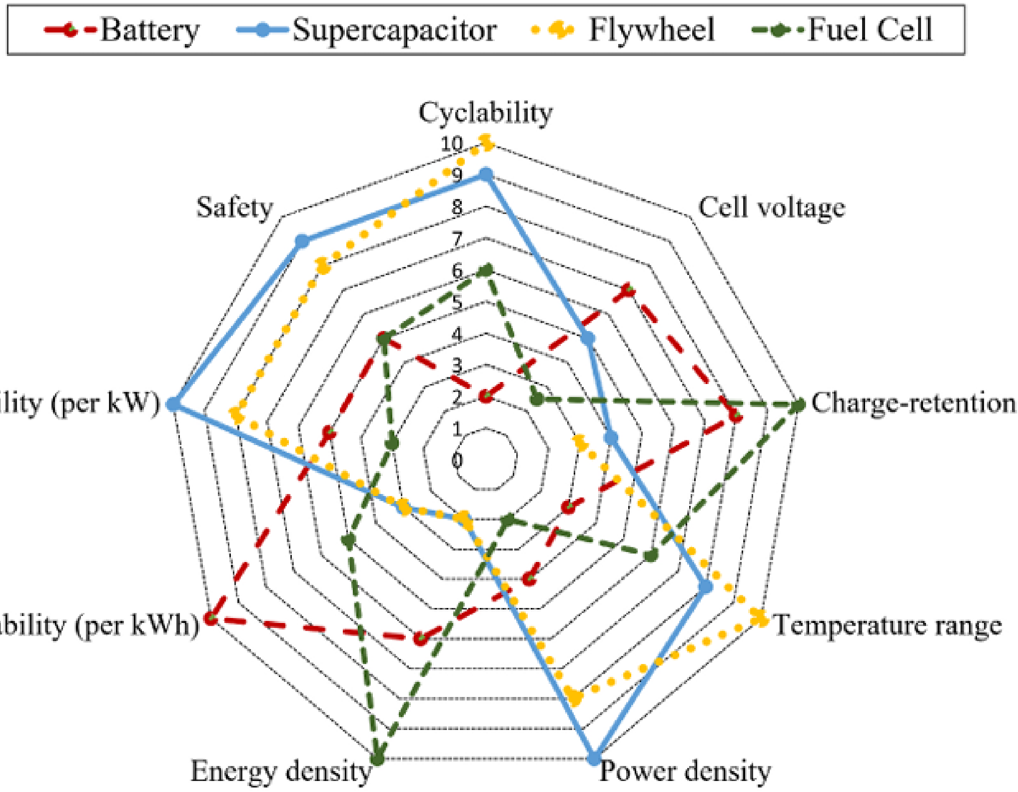

Figure 10 Qualitative comparison between different ESSs [29]. Reproduced with permission from ref 29. Copyright 2022, Elsevier Ltd.

6. SUPERCAPACITORS & THEIR MECHANISMS

A capacitor is an electrical component that stores energy by accumulating electric charges on two conductive surfaces separated by an insulating material, known as the dielectric. The ability of a capacitor to store charge at a given potential is referred to as its capacitance [30]. Capacitors are broadly categorized into Conventional Capacitors (CCs) and Supercapacitors (SCs). CCs, such as ceramic, electrolytic, and glass capacitors, store energy in an electric field and are commonly used in electronic circuits for functions like filtering, coupling, and energy buffering. In contrast, SCs store energy through electrostatic charge separation at the electrode–electrolyte interface. They bridge the gap between traditional capacitors and batteries by offering high power density and rapid charge/discharge capabilities [31].

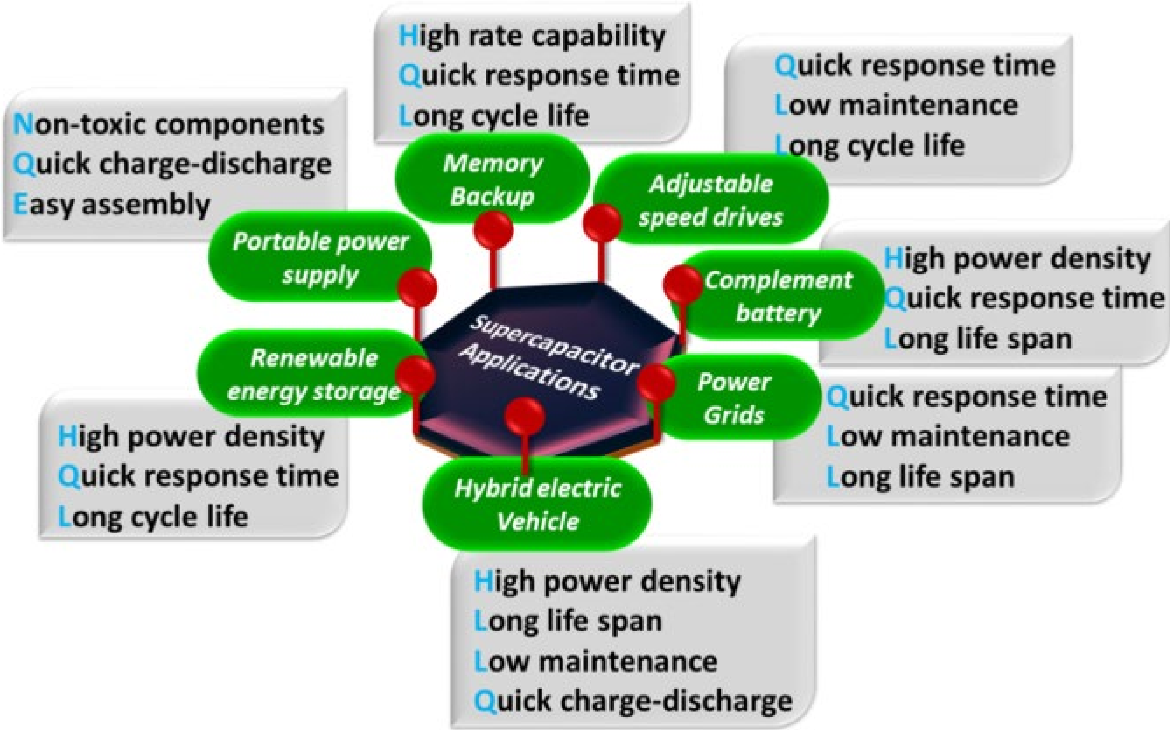

Figure 11 Supercapacitor applications [27]. Reproduced with permission from ref 27. Copyright 2025, Elsevier Ltd.

Due to excellent intrinsic characteristics, indicated in Figure 11, supercapacitors are employed in a wide range of applications due to their unique advantages. While every energy storage system (ESS) has its strengths and limitations, SCs stand out in several aspects. For example, batteries often suffer from a limited operating temperature range, low power density, and degradation under high power pulses. Flywheels, though effective, are hindered by high self-discharge rates and elevated installation costs. In contrast, SCs offer benefits such as lightweight design, stable efficiency across the operating range, and aging characteristics that are independent of the duty cycle.

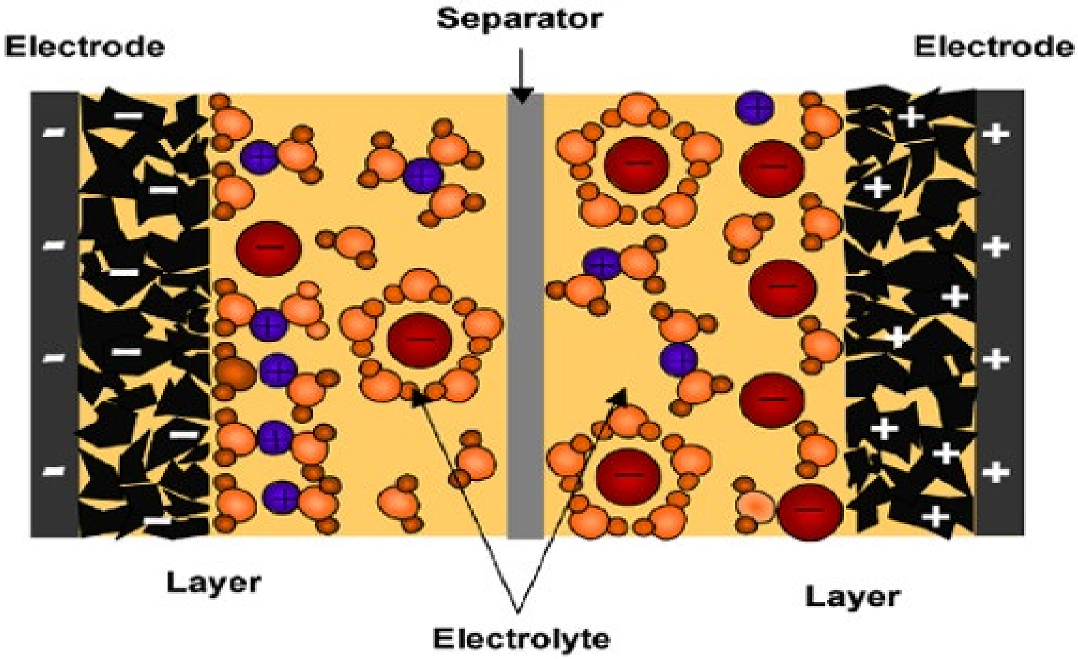

Figure 12 Structure of the supercapacitor as an energy storage device [29]. Reproduced with permission from ref 29. Copyright 2022, Elsevier Ltd.

As a result, SCs are particularly well-suited for applications requiring high power, low energy, and frequent charge/discharge cycles [31]. The construction of a supercapacitor, as illustrated in Figure 12, includes a separator, electrolyte, and two electrodes (current collectors). Structurally, it resembles an electrochemical battery, with the separator isolating the electrodes immersed in an electrolyte solution. However, the combination of the chosen electrodes and their engineering structure differs from that of the battery system.

Based on their charge storage mechanisms, supercapacitors are classified into three main types:

(a) Electric Double-Layer Capacitors (EDLCs)

(b) Pseudocapacitors (PCs)

(c) Hybrid Supercapacitors (HSCs)

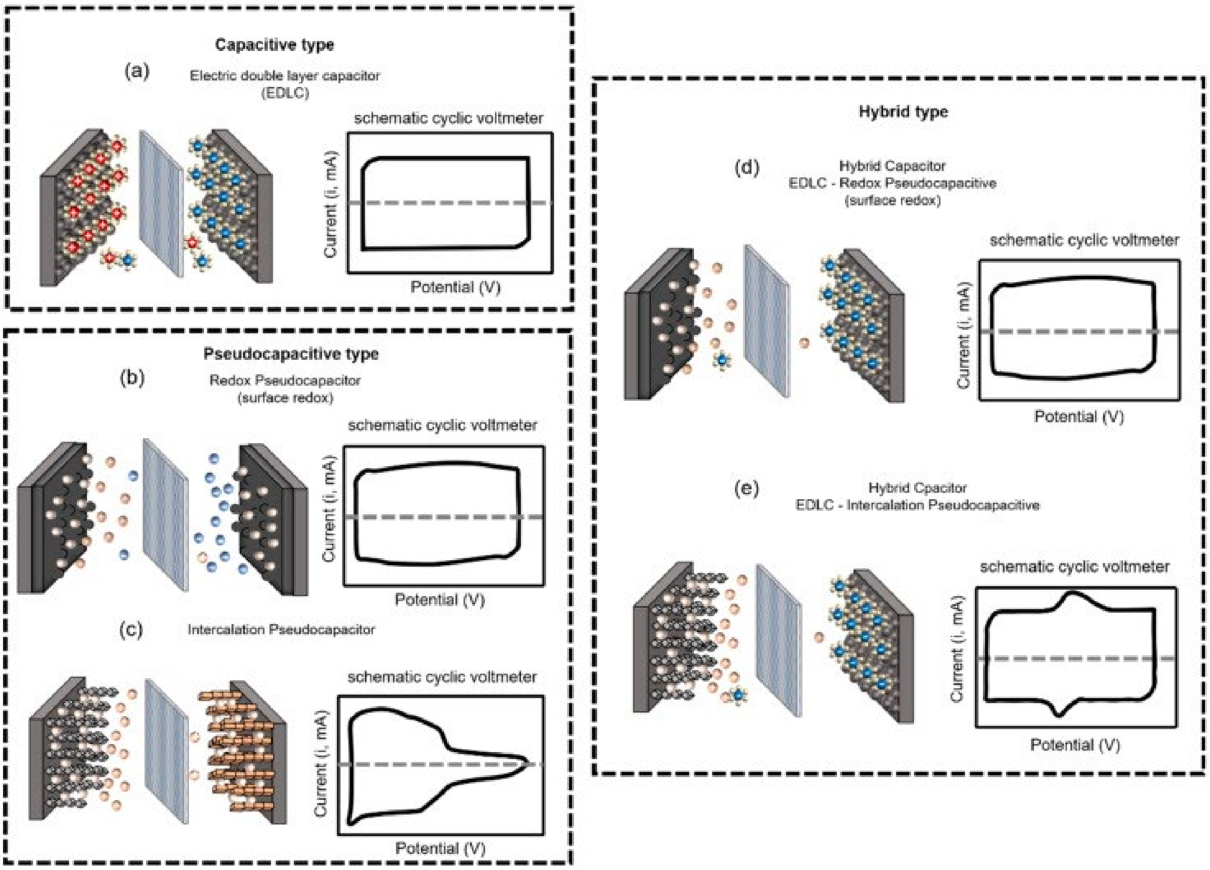

Figure 13 Classifications of Supercapacitors based on their mechanisms [32]. Reproduced from 32, open-access creative commons CC BY 4.0 license, MDPI

6.1 Electric double-layer capacitors (EDLCs)

Electric Double-Layer Capacitors (EDLCs) are a subclass of supercapacitors that store energy via electrostatic charge separation at the interface between an electrode surface and an electrolyte solution, without involving faradaic (redox) reactions, as schematically illustrated in Figure 13a. This mechanism enables EDLCs to achieve extremely fast charge/discharge rates and exceptional cycle life, often exceeding one million cycles. The electrodes are typically composed of high-surface-area carbon-based materials, such as activated carbon, carbon nanotubes, or graphene, which provide extensive surface area for double-layer formation. The amount of charge stored is directly proportional to the accessible surface area and inversely proportional to the distance between the ion layers and the electrode [31].

Due to their high-power density and rapid energy delivery, EDLCs are widely used in applications such as regenerative braking in hybrid vehicles, backup power in uninterruptible power supplies (UPS), and voltage smoothing in renewable energy systems. However, their relatively low energy density compared to batteries limits their suitability for long-duration energy storage. Ongoing research into nanostructured carbons, ionic liquid electrolytes, and hybrid capacitor designs aims to enhance their energy density while preserving their fast response and stability [33].

6.2 Pseudo-capacitors (PCs)

Pseudo-capacitors (PCs) are advanced electrochemical energy storage devices that bridge the gap between traditional capacitors and batteries by offering both high power and relatively high energy densities. Unlike EDLCs, which store charge electrostatically, PCs store energy through fast, reversible faradaic redox reactions occurring at or near the electrode surface (Figures 13 b–c). They are widely used in hybrid and electric vehicles (HEVs/EVs), portable electronics, grid stabilization, backup power systems, and wearable electronics [34].

PCs are categorized into intrinsic and extrinsic types based on their charge storage mechanisms:

Intrinsic pseudo-capacitors (e.g., hydrated RuO_2, MnO_2, Nb_2O_5), Figure 13b, exhibit capacitive behavior due to surface-confined redox reactions, independent of nanostructure. These materials typically show rectangular cyclic voltammograms and triangular galvanostatic charge-discharge curves, indicating rapid and reversible kinetics. Their high specific capacitance, excellent rate capability, and long cycle life make them ideal for high-performance applications [35].

Extrinsic pseudo-capacitors (Figure 13c) use battery-type materials (e.g., Co_3O_4, $Ni(OH)_2$, $NiCo_2O_4$) engineered at the nanoscale to mimic capacitive behavior. Their performance depends on particle size, surface defects, and nanostructure, often showing redox peaks in cyclic voltammetry due to slower kinetics. While they offer higher energy storage, they may sacrifice power density due to diffusion limitations.

Both types are critical for next-generation energy storage, with ongoing research focused on optimizing structure, conductivity, and interfacial engineering to balance energy density, power density, and stability [33].

6.3 Hybrid Supercapacitors (HSCs)

Hybrid Supercapacitors (HSCs), illustrated in Figures 13d–e, combine the electrostatic storage of EDLCs with the faradaic mechanisms of pseudo-capacitors or batteries, offering a balance between high energy and power densities. They are commonly used in electric vehicles, grid storage, and industrial equipment [33].

HSCs are classified into three main types:

- **Composite HSCs** integrate carbon materials with metal oxides in a single electrode, leveraging the conductivity of carbon and the redox activity of metal oxides. This synergy enhances specific capacitance, cycling stability, and conductivity. However, challenges such as thick oxide coatings or nanowhisker formation can hinder ion diffusion, necessitating careful material selection and electrolyte optimization [36].
- **Asymmetric HSCs** (Figure 13d) use two dissimilar electrodes—typically a carbon-based EDLC electrode and a battery-type electrode (e.g., lead dioxide, nickel oxyhydroxide, lithiated graphite, or lithium titanate). This configuration combines fast capacitive storage with high-capacity redox reactions. While traditional designs are limited by electrolyte volume, newer rocking-chair-type systems improve efficiency by minimizing electrolyte use and enhancing ion shuttling [37].

- **Battery-type HSCs** (Figure 13e) employ battery-like electrodes that store charge via intercalation, achieving higher energy densities than conventional supercapacitors. However, their slower kinetics can limit power output. With optimized electrode design and balanced kinetics, these hybrids offer a promising solution to bridge the gap between batteries and supercapacitors, delivering long life, safety, and substantial energy storage [36].

Figure 13 presents schematic cyclic voltammetry (CV) curves for each type, highlighting the transition from capacitive to battery-like behavior. Figure 14 further illustrates ion movement and mechanisms, aiding in the selection of appropriate materials for specific supercapacitor technologies.

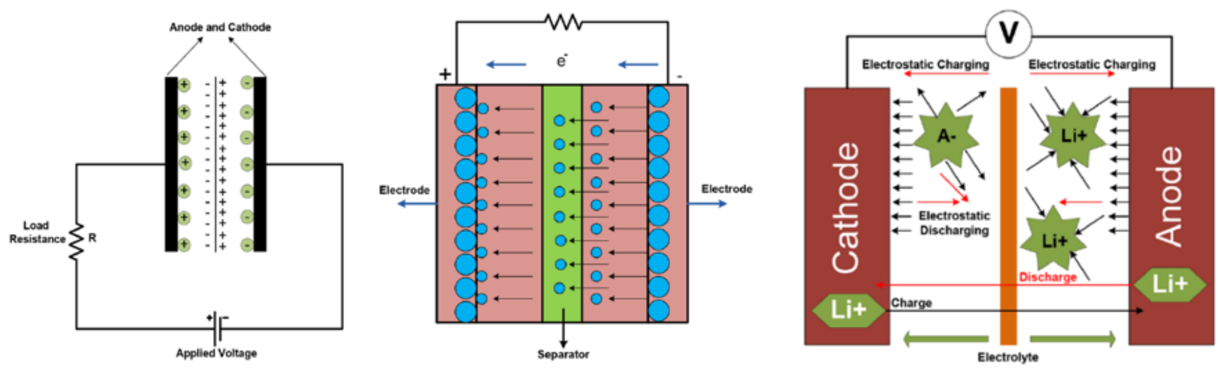

Figure 14 Schematic of EDLCs (left), PC (middle), and HSCs (right) [31]. Reproduced with permission from ref 31. Copyright 2022, Elsevier Ltd.

6.4. HSCs-based on BTMOs vs. BMOs

Hybrid (asymmetric) supercapacitors represent a compelling approach to energy storage by combining a Faradaic, battery-type electrode with a capacitive carbon-based electrode. This configuration allows each electrode to operate within distinct potential windows, enabling the full cell to achieve a higher operating voltage than symmetric electric double-layer capacitors (EDLCs). Since energy scales with the square of voltage ($E \propto V^2$), this design significantly enhances energy density while maintaining high power output and a long cycle life.

In typical hybrid systems, a redox-active positive electrode, often based on Binary Transition Metal Oxides (BTMOs) such as $NiMoO_4$, $CoMoO_4$, $MnMoO_4$, or their composites, is paired with a mostly capacitive negative electrode, commonly derived from activated carbon or graphene. BTMOs are attractive due to their multiple valence states, which enable high specific and areal capacitance and strong rate performance. Their electrochemical behavior benefits from nanoscale architectures (e.g., sheets, rods, mesoporous networks) and conductive scaffolds such as graphene, carbon nanotubes (CNTs), foams, or MXenes, which facilitate ion/electron transport and enhance cycling stability [38]. Additional improvements arise from defect engineering, including oxygen vacancies and cation doping, which accelerate charge transfer and improve conductivity. Despite these advantages, BTMOs face several challenges: modest intrinsic conductivity, structural degradation under deep cycling, limited voltage windows in aqueous electrolytes, and performance losses at practical mass loadings. These limitations can be mitigated through engineered porosity and tortuosity, which preserve short transport paths and maintain high areal performance. BTMO-based hybrids are well-suited for high-power applications such as buffering, pulse power delivery, rapid energy capture in mobility solutions, and integration with batteries for renewable energy smoothing and uninterruptible power supply (UPS) functions [39].

Binary Metal Oxide (BMO) hybrids [39], particularly alkaline-earth-based molybdate compounds like $MgMoO_4$, and scheelite-type $AMoO_4$ (e.g., $BaMoO_4$), offer similar benefits with distinct structural and electrochemical characteristics. These materials exhibit high theoretical capacities in alkaline electrolytes due to the redox activity of both the alkaline-earth metal and molybdenum centers. However, their wide band gaps necessitate hybridization with conductive materials such as reduced graphene oxide (rGO), CNTs, or MXenes to enhance charge transport. Like BTMOs, BMOs require nanoscale design strategies to overcome conductivity and rate limitations, particularly at high mass loadings [40].

For both BTMO and BMO systems, device-level considerations are critical. Thin laboratory coatings often overstate performance; practical electrodes must achieve high mass loadings (≥10 mg cm^{-2} or ~150–200 µm thickness) while maintaining low ionic and electronic resistance [40]. Effective fabrication techniques include growing oxides on 3D conductive foams, constructing hierarchical porosity, aligning internal channels, and targeted doping to improve redox kinetics and conductivity. Reliable performance metrics, such as areal capacitance, rate capability at high loading, and long-cycle stability, are essential for meaningful comparisons and real-world applicability.

Ultimately, the most promising route for scalable hybrid supercapacitors involves pairing redox-rich metal molybdates with engineered conductive frameworks, such as MXene-oxide or rGO/CNT-oxide hybrids and validating performance at commercial mass loadings [40-41]. Addressing remaining bottlenecks, such as longer diffusion paths, increased polarization, and electrolyte selection (aqueous vs. organic/ionic), will be key to positioning oxide-based hybrid supercapacitors as cost-effective, high-performance solutions for renewable energy integration, grid support, and electric mobility.

7. Role of electrode materials on the capacitance of supercapacitors (SCs)

The capacitance of supercapacitors (SCs) is strongly influenced by the properties of their electrode materials, including surface area, electrical conductivity, porosity, and electrochemical stability. As such, both electrodes and electrolytes are key components that can be engineered to enhance the overall performance of SCs. Modifying elements such as binders, electrode materials, separators, and electrolyte solutions can significantly improve energy storage capabilities [33]. The key factors that determine the supercapacitor performance are shown in Figure 15.

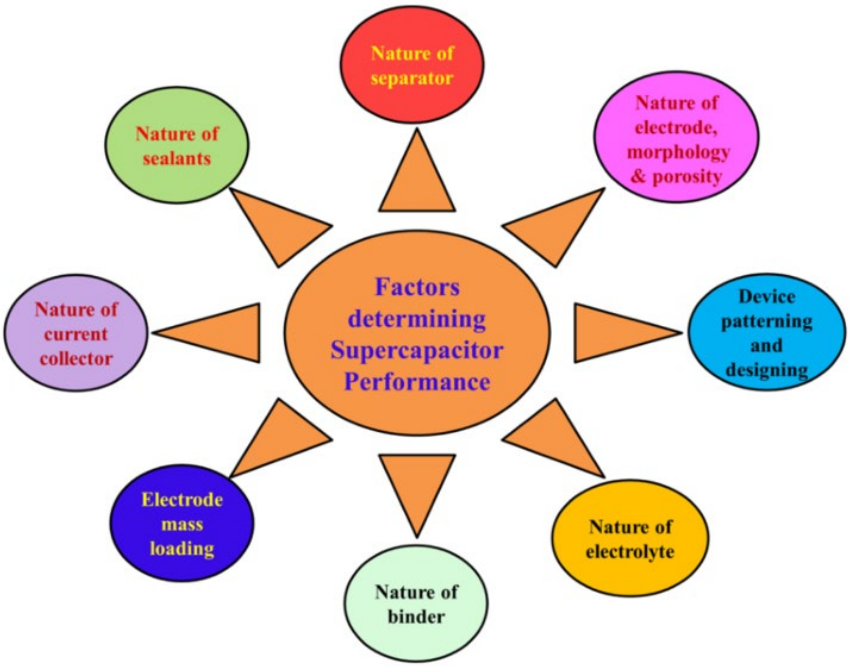

Figure 15 Nature of the electrode as one of the key factors in determining the supercapacitor performance [27]. Reproduced with permission from ref 27. Copyright 2025, Elsevier Ltd

Among the various factors influencing electrochemical performance, the choice of electrode material plays a pivotal role. In electric double-layer capacitors (EDLCs), enhancing energy density can be achieved by either increasing the specific capacitance or expanding the operating voltage window. While the electrolyte's dielectric properties primarily influence capacitance, the electrode material contributes significantly by providing a high surface area and an optimized pore structure that facilitates efficient ion adsorption. An increase in the effective surface area directly correlates with higher specific capacitance, thereby improving energy density. However, pores smaller than the solvated ion size (typically <1 nm) are inaccessible to ions and thus electrochemically inactive. These sub-nanometer pores not only fail to contribute to capacitance but may also impede ion transport, ultimately compromising overall device performance [33].

Advanced materials such as carbon nanotubes (CNTs), graphene, transition metal oxides (typically semiconducting with moderate conductivity), and conducting polymers are widely employed in supercapacitor electrodes due to their high surface area, favorable electrochemical properties, and ability to undergo rapid and reversible redox reactions. These characteristics enable efficient charge storage and fast ion/electron transport, making them integral to the development of high-performance energy storage devices [32]. Optimizing material properties such as particle size, porosity, and conductivity is essential for achieving high energy and power densities. Equally important is the mechanical and chemical stability of electrode materials, which affects the cycling life and durability of the device. Materials that maintain structural integrity during repeated charge–discharge cycles ensure long-term performance. Pseudocapacitive materials with strong chemical resistance and mechanical flexibility offer enhanced cycle stability, while highly conductive materials minimize resistive losses, crucial for high power output.

To further improve electrochemical performance, techniques such as doping, compositing, and surface modification are commonly employed. These approaches enhance charge transfer kinetics and the reversibility of redox reactions. Thus, the careful selection, design, and engineering of electrode materials are vital for maximizing supercapacitor efficiency and meeting the growing demand for high-performance energy storage systems.[32]. Activated carbon remains a widely used electrode material due to its high surface area and cost-effectiveness, though its energy density is relatively limited. To overcome this, materials such as RuO_2, MnO_2, conductive polymers, and emerging 2D materials like graphene and MXenes are being explored for their superior capacitance and energy density. However, challenges such as high cost, low conductivity, and limited cycling stability continue to hinder their widespread adoption.[42].

7.1. Role of Transition Metal Cations and their valence states

Transition metal oxides and cations represent a diverse class of materials characterized by the bonding of transition metals with oxygen. These compounds exhibit a broad spectrum of electronic, magnetic, and catalytic properties, primarily due to their variable oxidation states and adaptable crystal structures [43]. Transition metal cations are particularly instrumental in enhancing the electrochemical performance of supercapacitors, as they enable multiple, reversible redox reactions that are essential for efficient energy storage [44].

Oxides of transition metals such as cobalt, nickel, manganese, zinc, and vanadium possess rich multivalent oxidation states (e.g., Co^{2+}/Co^{3+}, Ni^{2+}/Ni^{3+}), which facilitate Faradaic charge storage mechanisms. This significantly contributes to high specific capacitance and energy density. Their ability to undergo rapid and reversible redox transitions with minimal structural degradation ensures excellent cyclic stability and rate capability. As a result, transition metal-based electrodes serve as a critical bridge between capacitive and battery-like behaviors in hybrid energy storage devices, offering a promising route toward the development of high-performance and long-lasting systems [45]. Moreover, transition metal cations support charge storage not only at the electrode surface but also within the bulk material through ion insertion and diffusion processes, thereby enhancing pseudocapacitance.

Materials such as NiO, Co_3O_4, and ZnO, with their multiple accessible oxidation states, enable these redox transitions, leading to improved electrochemical performance, specific capacitance, and cycle life. Their structural versatility, environmental benignity, and natural abundance further position transition metal oxides as leading candidates for next-generation energy storage technologies [46]. Transition metal cations, originating from elements in groups 3 to 12 of the periodic table, exhibit unique performance characteristics that make them highly valuable in a wide range of electrochemical and catalytic applications, particularly in batteries and supercapacitors. The following section, tabulated in Table 1, summarizes their key performance attributes.

Table 1 *Performance characteristics of transition metal/bivalent cations for energy storage devices*

Transition Metal Cation	**Oxidation States/Redox Couples**	**Specific Capacity/Capacitance**	**Voltage Window (V)**	**Cycling Stability**	**Fabrication Method**	**Mass Loading (mg/cm²)**	**Limitations**
Mn ($Mn^{2+}/Mn^{3+}/Mn^{4+}$) [47]	Multi-electron redox	~120 mAh/g	3.0-4.0	Prone to dissolution unless stabilized	Hydrothermal, sol-gel, electrodeposition	1-3	Structural distortion (Jahn-Teller effect)
Co (Co^{2+}/Co^{3+}) [47]	Reversible redox	~140 mAh/g	3.8-4.0	Good stability but costly/toxic	Hydrothermal, CVD, electrodeposition	1-2	Limited scalability due to cost
Ni ($Ni^{2+}/Ni^{3+}/Ni^{4+}$) [48-49]	$Ni^{2+} \rightarrow Ni^{3+}/Ni^{4+}$	~200 mAh/g	3.7-4.8	Good, requires stabilization	Hydrothermal, electrodeposited nanosheets	2-5	High-voltage instability without coatings
Fe (Fe^{2+}/Fe^{3+}) [48-49]	Fe^{3+}/Fe^{2+}	160–170 mAh/g	~3.4	Excellent (thousands of cycles)	Solid-state, sol-gel, spray pyrolysis	1-3	Needs conductive additives for better conductivity
V ($V^{3+}/V^{4+}/V^{5+}$) [50-51]	Multi-redox	100–150 mAh/g	Up to 4.8	Moderate stability	Hydrothermal, CVD	1-2	Prone to structural degradation at high voltage
Cu ($Cu^{2+}/Cu^{+}/Cu^{0}$) [52-53]	Conversion redox	375–670 mAh/g	1.7-2.2	Poor–moderate	Hydrothermal, electrodeposition	2-4	Severe volume change during cycling
Ti (Ti^{4+}) [54]	Ti^{4+}/Ti^{3+}	~230 mAh/g	2.2	Stable (>1000 cycles)	Hydrothermal, sol-gel	1-2	Lower voltage, but excellent cycling
Zn (Zn^{2+}) [55-56]	EDLC + redox	Up to 436 F/g	0.2-1.8	Excellent (>6000 cycles)	Hydrothermal, electrodeposited foams	1-5	Promising for hybrid SCs
Mg (Mg^{2+}) [57-58]	Pseudocapacitive	~230 F/g	0-1.7	Stable (>2000 cycles)	Sol-gel, solid-state	1-3	Bivalent nature improves storage

7.2. Binary Transition Metal Oxides vs. Binary Metal Oxides

Binary transition metal oxides (BTMOs), composed of two different transition metals (such as Ni, Co, Fe, Mn, or V) combined with oxygen, have gained significant attention as advanced electrode materials for supercapacitor applications due to their enhanced electrochemical properties. BTMOs synergistically utilize the multiple redox states of two metal ions, leading to superior specific capacitance, energy density, and cycling stability compared to single-metal oxides. Their strong structural integrity, improved electronic conductivity, and abundant active redox sites enable faster ion and electron transport, making them highly suitable for rapid charge-discharge processes in supercapacitors [59].

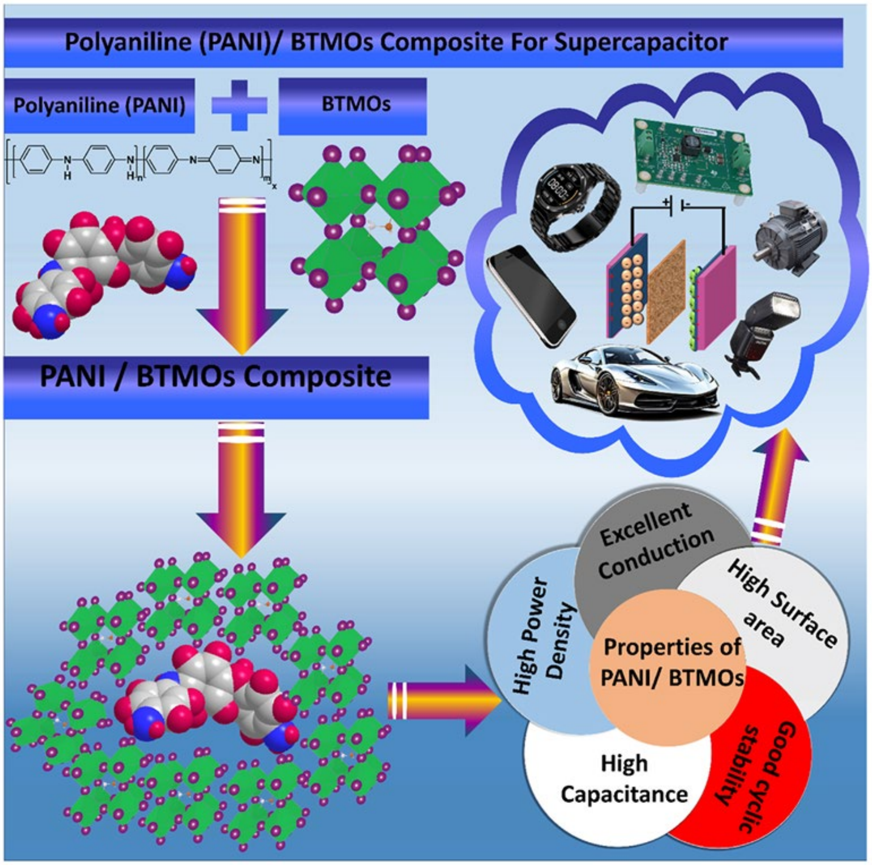

Figure 16 Graphical representation of synthesis, properties, and versatile applications of PANI/BTMOs in supercapacitors [60]. Reproduced with permission from ref 60. Copyright 2025, Elsevier Ltd.

Figure 16 presents a graphical overview of the synthesis strategies, electrochemical mechanisms, and diverse energy storage applications of PANI/BTMO composites, including hybrid supercapacitors, wearable electronics, and electrocatalysis. Polyaniline (PANI), a widely studied conducting polymer, has attracted considerable attention in supercapacitor research due to its high theoretical specific capacitance, excellent electrical conductivity, and cost-effectiveness. Structurally, PANI exists in multiple oxidation states—leucoemeraldine, emeraldine, and pernigraniline—with emeraldine being the most electroactive form. This form facilitates efficient charge storage through rapid and reversible redox reactions along the polymer backbone. Despite its advantages, pristine PANI suffers from poor cycling stability and limited surface area, which constrain its standalone performance. To address these limitations, PANI is often engineered into nanostructures or integrated with binary transition metal oxides (BTMOs). These nanocomposites exhibit enhanced capacitance, improved rate capability, and greater electrochemical stability [60].

Similarly, binary metal oxides (BMOs), composed of two distinct metal elements, typically a bivalent alkaline earth metal and a transition metal in the form of molybdate within an oxide framework, have emerged as highly promising electrode materials for supercapacitor applications. BMOs of the ABO_4 class, where "A" and "B" represent elements with oxidation states of +2 and +6, respectively, form a versatile family of inorganic compounds with broad applicability in energy storage. For instance, "A" commonly denotes alkaline earth metals such as calcium or barium, while "B" often refers to molybdenum (Mo). ABO_4-type BMOs such as $CaMoO_4$, $SrMoO_4$, and $BaMoO_4$ crystallize in the scheelite structure, characterized by tetrahedral coordination of Mo atoms. While $MgMoO_4$ crystallises in the wolframite-monoclinic structure, it is characterised by the octahedral coordination of Mo atoms, as it depends on the size and electronegativity of the A cation.

The synergistic interaction between multiple metal cations in these BMOs enhances electrical conductivity and promotes the formation of oxygen vacancies, both of which are critical for rapid ion transport and efficient charge storage. Notably, scheelite-type molybdates with the same divalent metal exhibit complete mutual solubility across the compositional range, resulting in a rich family of solid-state solution compounds. Furthermore, incorporating TMOs into nanocomposites with carbon-based materials increases surface area and optimizes porosity, thereby improving electrochemical performance. The presence of multiple oxidation states in BMOs facilitates richer and more reversible redox reactions, significantly boosting specific capacitance, energy density, and cycling stability compared to single-metal oxide counterparts [61].

In typical BTMOs, both cations are transition metals (such as in $NiCo_2O_4$ or $CuMn_2O_4$), enabling rich, multi-electron redox activity from both elements. However, BMOs such as $BaMoO_4$ (Barium Molybdate) only have molybdenum belongs to the transition metal series, whereas barium is an alkaline earth metal. Despite this distinction, $BaMoO_4$ remains a highly attractive electrode material for supercapacitor applications due to molybdenum's variable oxidation states (Mo^{6+}/Mo^{5+}) that facilitate fast, reversible redox reactions, while barium contributes to structural robustness and stability during cycling. As a result, $BaMoO_4$-based electrodes offer a valuable balance of high electrochemical activity, excellent cyclic stability, and chemical durability, positioning them as promising candidates for next-generation energy storage devices [62-63].

Over the years, bimetallic molybdates (BTMOs) such as $NiMoO_4$, $CoMoO_4$, $MnMoO_4$, $CuMoO_4$, and $ZnMoO_4$ have garnered significant attention as advanced electrode materials for supercapacitors due to their rich redox behavior, structural tunability, and high theoretical capacitance [61]. The performance of various molybdate frameworks in a two-electrode system using nitrogen-doped graphene oxide carbon nanotube composites (NrGO/CNT) as anode is shown in Figure 17. Among these, $NiMoO_4$ has demonstrated outstanding electrochemical performance delivering capacitance of 261 $F.g^{-1}$ for an asymmetric device, primarily attributed to the synergistic redox interactions between Ni^{2+}/Ni^{3+} and Mo^{6+} ions. Whereas $MnMoO_4$ and $CuMoO_4$ exhibited a distorted rectangular CV profile. Regardless of the cations, all the CV profiles show EDLC behaviour, and the characteristic feature of pseudocapacitance (redox-like curves) is absent.

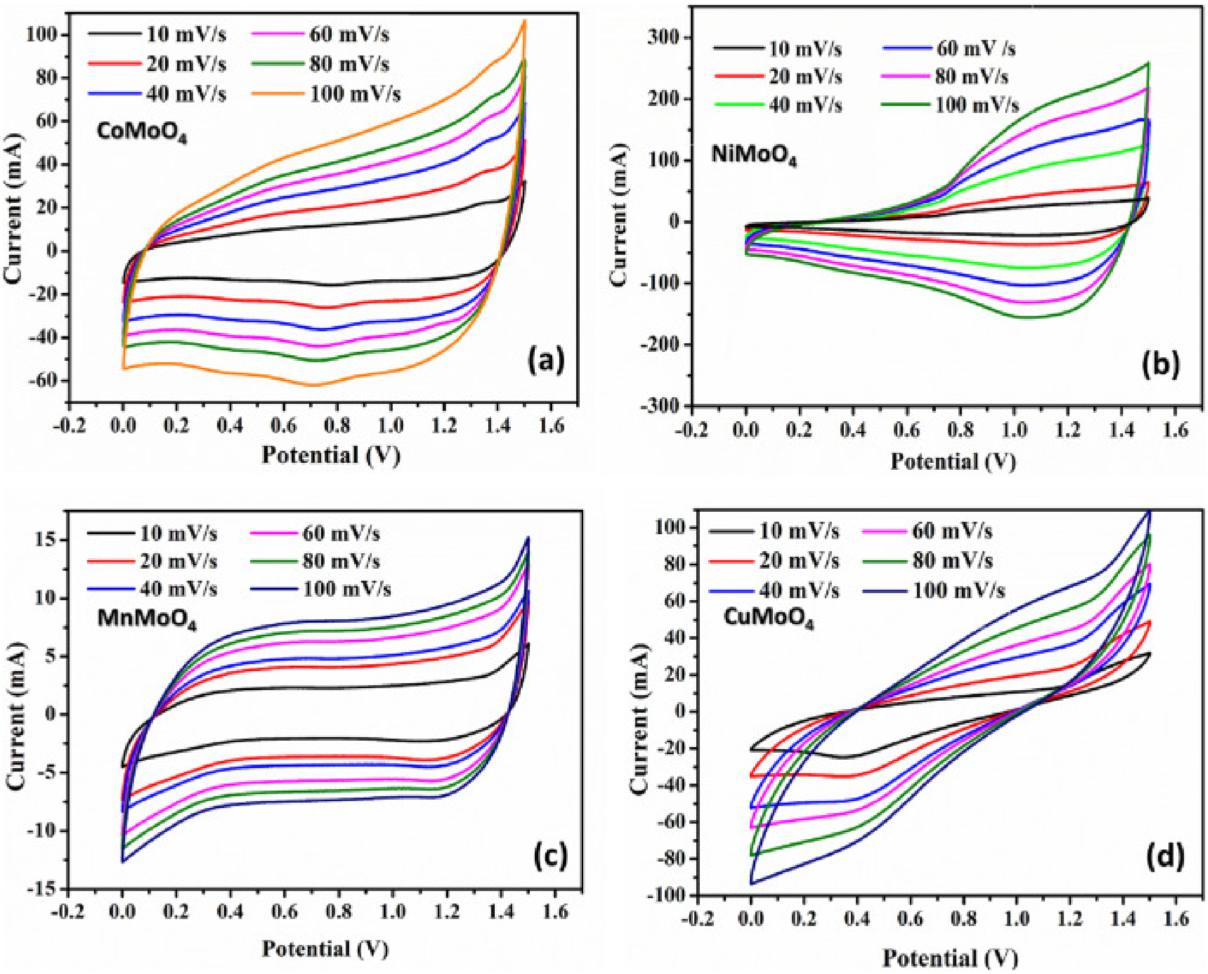

Figure 17 Cyclic voltammetry curves of (a) $CoMoO_4$, (b) $NiMoO_4$, (c) $MnMoO_4$, and (c) $CuMoO_4$ with the respective sweep rates indicated in the plots [61]. Reproduced with permission from ref 61. Copyright 2024, Elsevier Ltd.

Besides the selection of cations, nanostructure engineering has also been reported as an effective strategy to enhance the electrochemical energy storage properties [64]. For instance, the honeycomb-like $NiMoO_4$ ultrathin nanosheet arrays deliver a high specific capacitance of 1694 F g^{-1} at 1 A g^{-1}, with excellent rate capability (72% retention up to 50 A g^{-1}) and remarkable cycling stability (92.7% retention after 9000 cycles) [64]. Such superior performance is largely due to the nanosheet morphology, which enhances ion diffusion and electron transport pathways. Similarly, $CoMoO_4$ exhibits strong pseudocapacitive behaviour due to the Co^{2+}/Co^{3+} redox couple. It was reported that $CoMoO_4$ nanosheet electrodes synthesized on nickel foam demonstrate superior pseudocapacitive behaviour, characterized by a high areal specific capacitance of 1120 mF/cm² at 4 mA/cm², retaining excellent stability over 3000 charge–discharge cycles with negligible capacitance loss. The system exhibits strong faradaic charge storage due to Co^{2+}/Co^{3+} redox transitions, minimal internal resistance (< 2 Ω), and stable electrochemical behaviour, highlighting its viability for high-performance supercapacitor applications [65].

However, $MnMoO_4$ offers a more environmentally benign and cost-effective option, among molybdate-based electrode materials, although its performance is relatively moderate. For instance, electro-spun porous $MnMoO_4$ nanotubes have demonstrated a specific capacitance of 620 F/g at 1 A/g, retaining 460 F/g even at 60 A/g, with only 9% loss after 10,000 cycles. Their hollow, mesoporous structure facilitates rapid ion transport and contributes to high electrochemical stability. An asymmetric device based on these nanotubes achieved a maximum energy density of 31.7 Wh/kg and a power density of 797 W/kg [66]. In contrast, zinc molybdate ($ZnMoO_4$), while not exhibiting classical transition-metal redox behavior on its own, offers excellent structural integrity and favorable morphology, making it a valuable stabilizing component in hybrid electrode systems. For example, a $ZnMoO_4$@$ZnCo_2O_4$ nanosheet composite has shown an impressive specific capacitance of 1,903 F/g at a current density of 1 A/g, along with excellent cycling stability, retaining 91% of its capacity after 5,000 cycles. These results underscore the synergistic benefits and durability of $ZnMoO_4$ when incorporated into composite electrode architecture [67].

Thus, these findings underscore the critical role of transition metal cations and their valence electron flexibility in determining energy storage performance. Among binary molybdates, $NiMoO_4$ and $CoMoO_4$ exhibit pseudocapacitive behaviour, while $MnMoO_4$ and $ZnMoO_4$ offer advantages in sustainability and structural reinforcement, respectively. As global resources are increasingly leveraged for diverse technological applications, alternative materials are being actively explored. In this context, bimetallic compounds such as barium molybdate ($BaMoO_4$) have shown promising potential as electrode materials, demonstrating adequate capability for enhancing energy storage performance [68].

Other BMOs, such as $AMoO_4$ (A = Mg, Ca, or Sr), have also attracted interest for supercapacitor applications. For example, $MgMoO_4$ nanosheets have demonstrated a specific capacitance of 200 F/g at a current density of 0.5 A/g, retaining 150 F/g at 5 A/g, indicating excellent rate capability. The proposed mechanism involves OH^- ions forming a double layer on the surface of $Mg(OH)_2$ and intercalating into Mg sites to form MgOOH [69]. As illustrated in the cyclic voltammetry (CV) and charge–discharge curves in Figure 18a-b, the profiles are reversible and stable within the applied potential window, contributing to the observed specific capacitance of 200 F/g. Furthermore, $MgMoO_4$ exhibits strong cycling stability, maintaining 92% of its initial capacitance after 1,000 cycles. Its low charge-transfer resistance suggests efficient ion transport and good electrical conductivity, reinforcing its suitability as a stable and efficient positive electrode, particularly in hybrid supercapacitor systems. In such configurations, activated carbon (AC) serves as the capacitive component, while $MgMoO_4$ functions as a pseudocapacitive material. The hybrid cell (Fig. 18c) operates at a voltage of approximately 1.6 V. Although the CV curve area for AC is larger than that of $MgMoO_4$, the

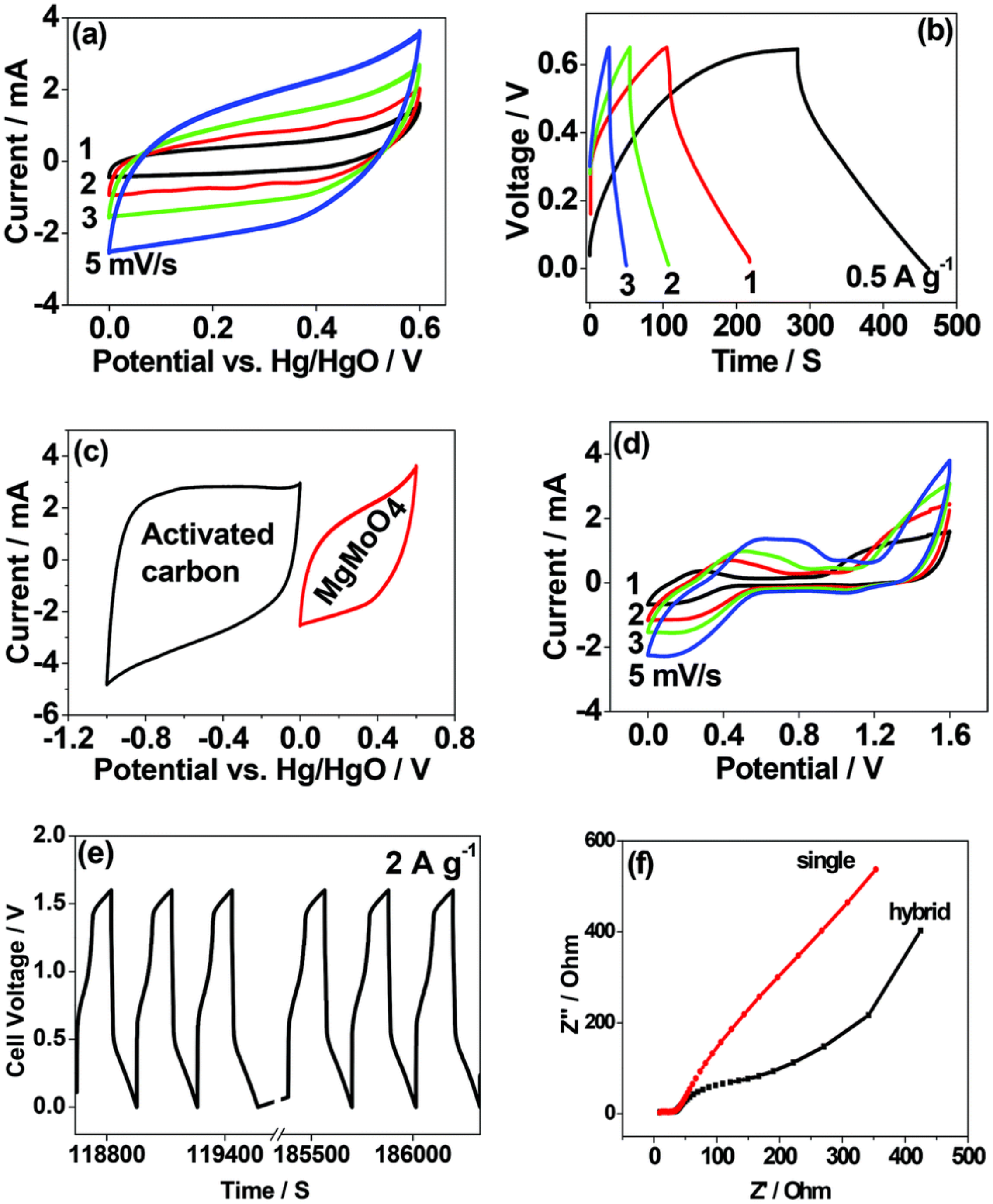

Figure 18 (a) First cyclic voltammetric (CV) curves, and (b) charge–discharge behaviour of the $MgMoO_4$ electrode. (c) CV curves of $MgMoO_4$ as positive compared with activated carbon as the negative electrode. Hybrid cell (d) CV and (e) charge–discharge curves of supercapacitors comprising AC‖$MgMoO_4$ in 2 M NaOH aqueous electrolyte. (f) Nyquist plot comparing the impedance in a high frequency region and capacitive behaviour in a low frequency region for single and hybrid cells. Sweep rates and current density are indicated in the respective figures [69]. Reproduced with permission from ref 69. Copyright 2018, Royal Society of Chemistry.

oxide benefits from an extended voltage window, enhancing its contribution as the positive electrode.

The typical $MgMoO_4$ is synthesised at room temperature, and a stable pressure phase crystallizes into a monoclinic structure (C2/m) formed by two octahedral [MgO_6] and two tetrahedral [MoO_4] sites. The lattice structure of $MgMoO_4$ is shown in Figure 19.

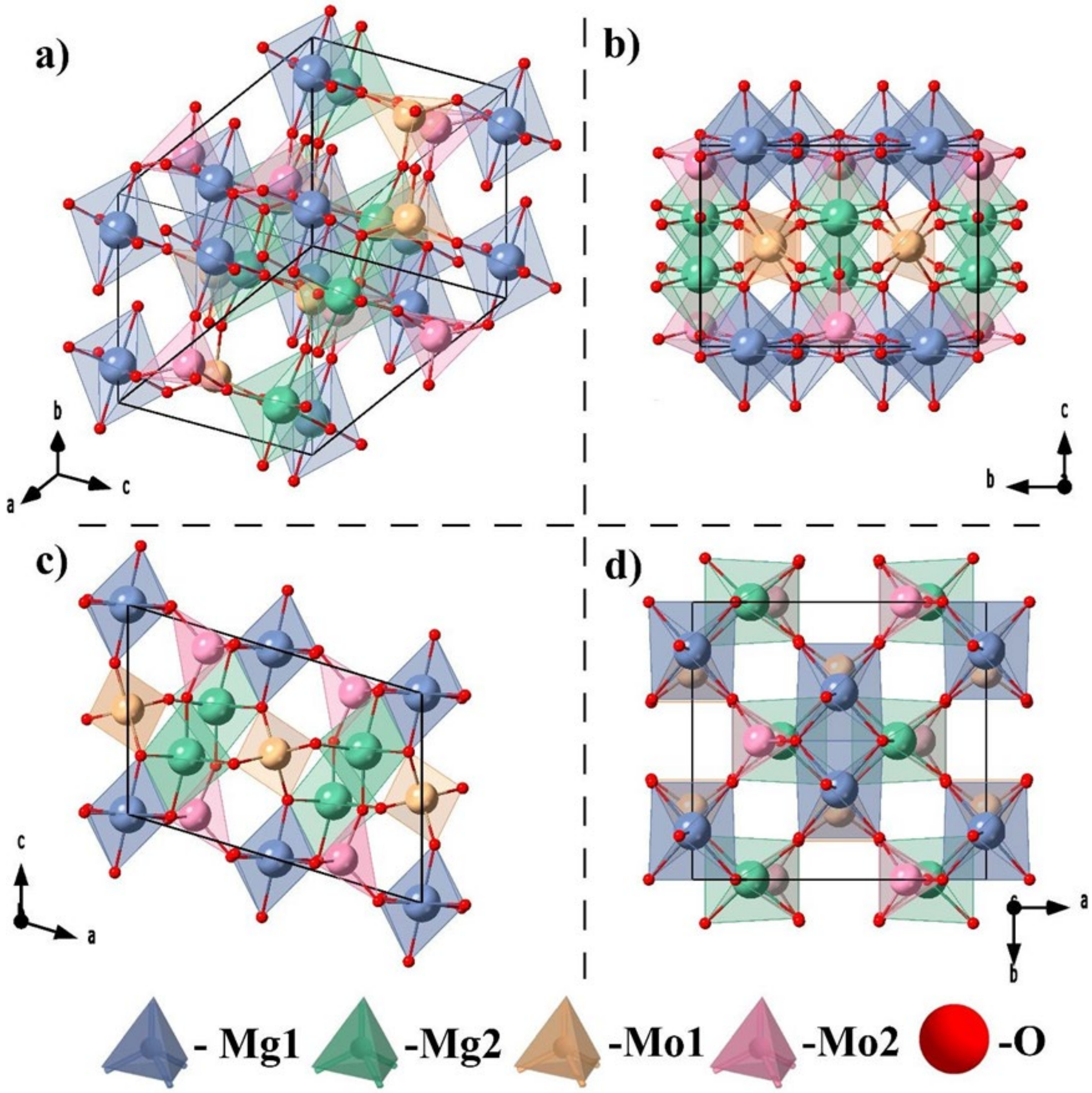

Figure 19 Schematic crystal structure of $MgMoO_4$ from the (a) standard orientation of crystal shape, (b) a-axis direction, (c) b-axis direction, and (d) c-axis direction [70]. Reproduced with permission from ref 70. Copyright 2020, American Chemical Society.

Similarly, calcium molybdate ($CaMoO_4$), another BMO, crystallizes in a powellite-type structure (Figure 20) at lower synthesis temperatures (around 300 °C), characterized by loosely connected molybdate ions in tetrahedral coordination with large bivalent cations. At elevated temperatures (≥ 600 °C), XRD analysis (Figure 21) reveals a structural transition from powellite to scheelite, suggesting that crystallinity influences phase transformation and enhances energy storage properties. $CaMoO_4$ exhibits several promising features for energy storage, including thermal stability, environmental compatibility, and cost-effectiveness. According to the reported work by Minakshi et al [71], $CaMoO_4$ nanoparticles achieved a specific capacitance of 110 F/g at 0.5 A/g and retained 85% of their initial capacitance after 1,000 charge–discharge cycles. The material also demonstrated low internal resistance and favorable redox activity, making it a suitable candidate for hybrid or composite supercapacitor systems. These findings suggest that $CaMoO_4$ can serve as a reliable and efficient electrode material, especially when enhanced with conductive additives to improve rate performance. especially when enhanced with conductive additives to improve rate performance.

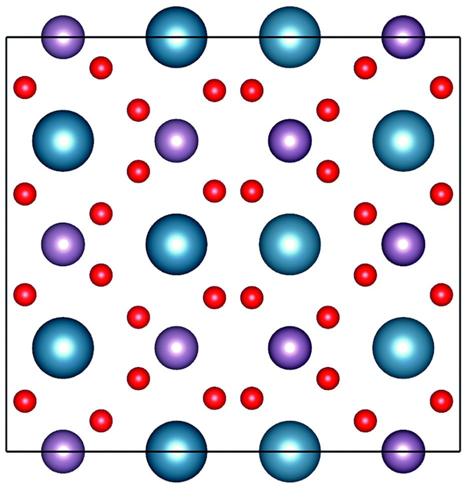

Figure 20 Representation of the powellite-type crystal structure of a typical BMO with a bivalent cation, Ca in $CaMoO_4$. The atoms with blue, pink, and red indicate Ca, Mo, and O, respectively [71]. Reproduced with permission from ref 71. Copyright 2019, Royal Society of Chemistry.

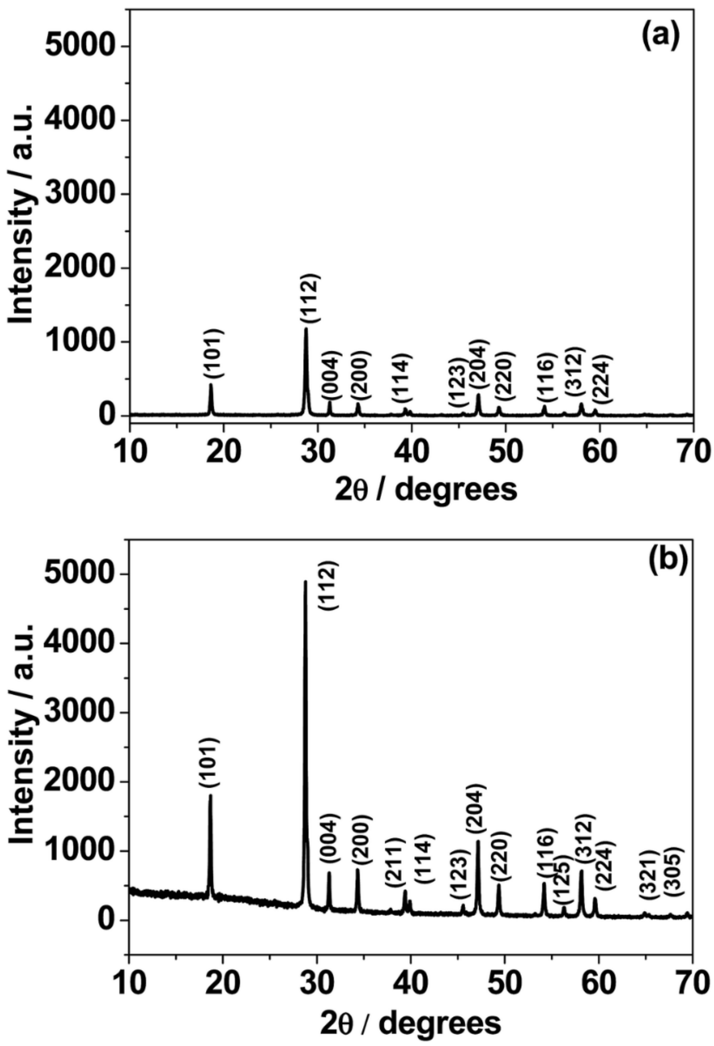

Figure 21 X-ray diffraction (XRD) patterns of BMO, such as $CaMoO_4$, synthesized at: (a) 300 and (b) 500 °C. The lower temperature material displayed a much weaker pattern, suggesting that it was not as crystalline as the higher temperature counterpart, forming a Scheelite structure [71]. Reproduced with permission from ref 71. Copyright 2019, Royal Society of Chemistry.

Recently, strontium-based barium molybdate ($SrMoO_4$) has been explored for energy storage applications. Synthesized via a simple wet chemical method, $SrMoO_4$ exhibits promising characteristics suitable for use in pseudocapacitors and battery-type devices. The compound crystallizes in a tetragonal structure and belongs to the scheelite-type materials group, characterized by the space group $I4_1/a$. In the typical unit cell of $SrMoO_4$, shown in Fig. 22, each molybdenum atom is coordinated by four oxygen atoms, forming a MoO_4 tetrahedron, while each strontium atom is surrounded by eight oxygen atoms, resulting in a distorted SrO_8 polyhedral configuration. For $SrMoO_4$, the calculated specific capacitance was reported to be 384 C/g at a scan rate of 5 mV/s [73], exhibiting a typical redox peak-like curve as shown in Figure 23. The electrochemical process begins with the interaction between Sr^{2+} ions in $SrMoO_4$ and OH^- ions in the electrolyte, forming strontium hydroxide. This is followed by a subsequent reaction with additional OH^- ions, yielding strontium oxyhydroxide. Notably, molybdenum ions in $SrMoO_4$ play a conductive role by enhancing the material's electrical conductivity, although they do not directly participate in redox reactions. This contribution is beneficial for improving charge transport and increasing specific capacitance.

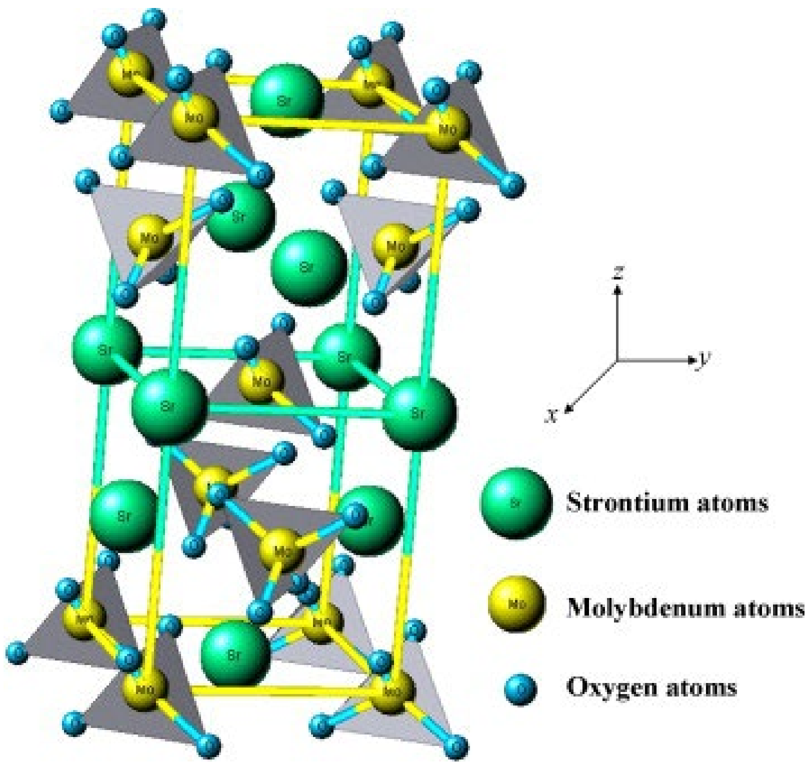

Figure 22 The unit cell of the strontium molybdate ($SrMoO_4$) crystallizes in a tetragonal structure [72]. Reproduced with permission from ref 72. Copyright 2024, Elsevier Ltd.

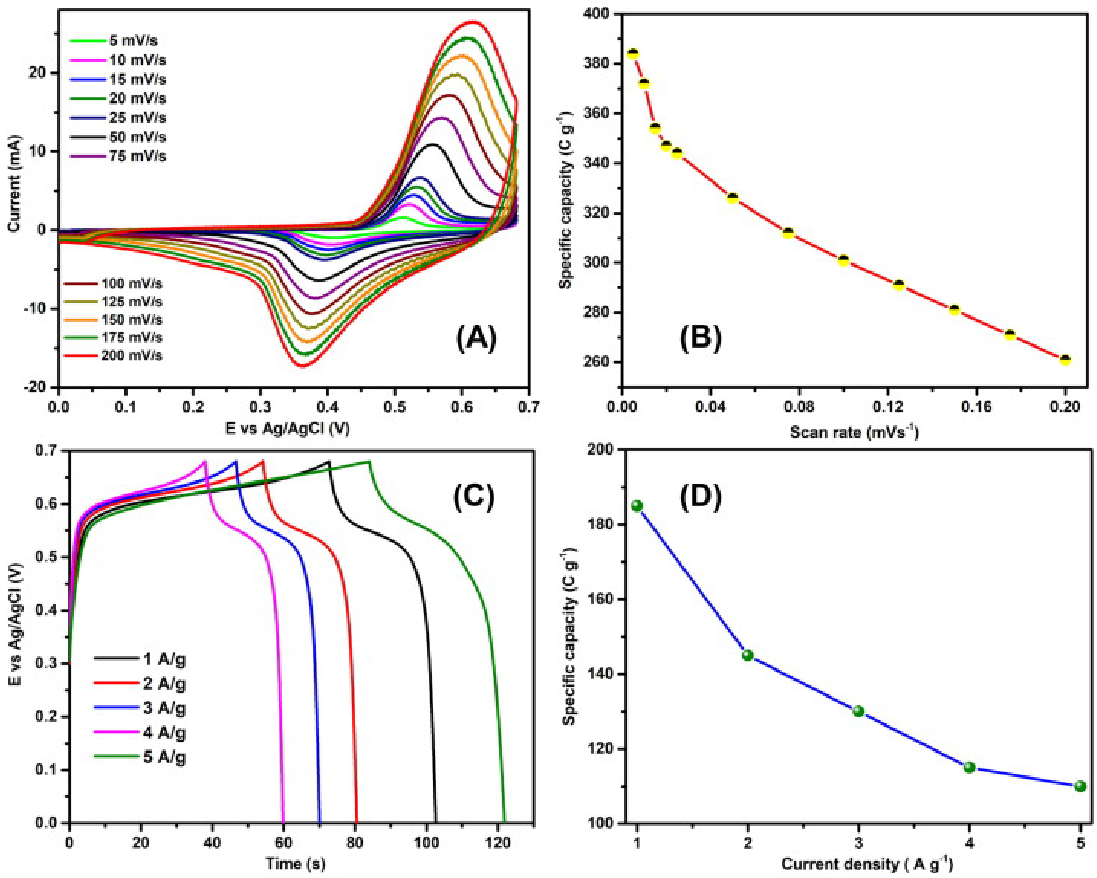

Figure 23 Cyclic voltammetric (CV) curves, (b) effect of scan rates, and (c) charge–discharge behaviour, (d) effect of current density of the $SrMoO_4$ electrode [73]. Reproduced with permission from ref 73. Copyright 2024, Elsevier Ltd.

Overall, the comparative electrochemical performance of binary transition metal oxides (BTMOs) and binary metal oxides (BMOs) is summarized in Table 2, demonstrating that ABO_4-type compounds [74-81] are competitive candidates for supercapacitor applications due to their structural versatility, conductivity, and redox behavior

Table 2 Comparison of electrochemical performance metrics of BTMOs and BMOs electrodes reported in the literature with those of ZnO-doped $BaMoO_4$

ABO_4 Material (BTMOs vs. BMOs)	Electrolyte	Current density (or) Scan rate	Specific Capacitance (F/g)	Cyclic Stability/retention	Reference
$NiMoO_4$	1M KOH	2 mA/cm^2	450	1000 / 94%	[74]
$CoMoO_4$	1M KOH	1 mA/cm^2	133	1000 / 100%	[75]
$CuMnO_4$	1M KOH	1 mA/cm^2	127	1000 / 82.5%	[76]
$MnMoO_4$	2M NaOH	0.5 mA/cm^2	168	2000 / 96%	[77]
$ZnMoO_4$	3M KOH	2 mV/s	487	4000 / 93.6%	[78]
$CoMoO_4$/ graphene	6M KOH	1 mV/s	394	500 / 39.8%	[79]
$MnMoO_4$/ $CoMoO_4$	2M NaOH	1 A/g	187	1000 / 98%	[80]
$MgMoO_4$	2M NaOH	1 mV/s	207	1000/98%	[69]
$CaMoO_4$	2M NaOH	2 A/g	118	6000 / -	[81]
$SrMoO_4$	1M KOH	5 mV/s	384 C/g	5000 / 91.1%	[68]
$BaMoO_4$	1 M KOH	1 A/g	79	1100 / 76.6%	
Sm-doped $BaMoO_4$	1 M KOH	1 A/g	135	5000 / 83.38%	[68]
ZnO-doped $BaMoO_4$	2M Na_2SO_4	1 mV/s	270	1000 / 98%	[82]

8. Barium Molybdate ($BaMoO_4$) for Energy Storage Applications

In recent years, among the BMOs stated earlier, $BaMoO_4$ has emerged as a promising component in the development of electrode materials for various energy storage applications. Its incorporation not only offers a viable alternative to conventional materials but also helps alleviate the pressure on increasingly scarce natural resources.

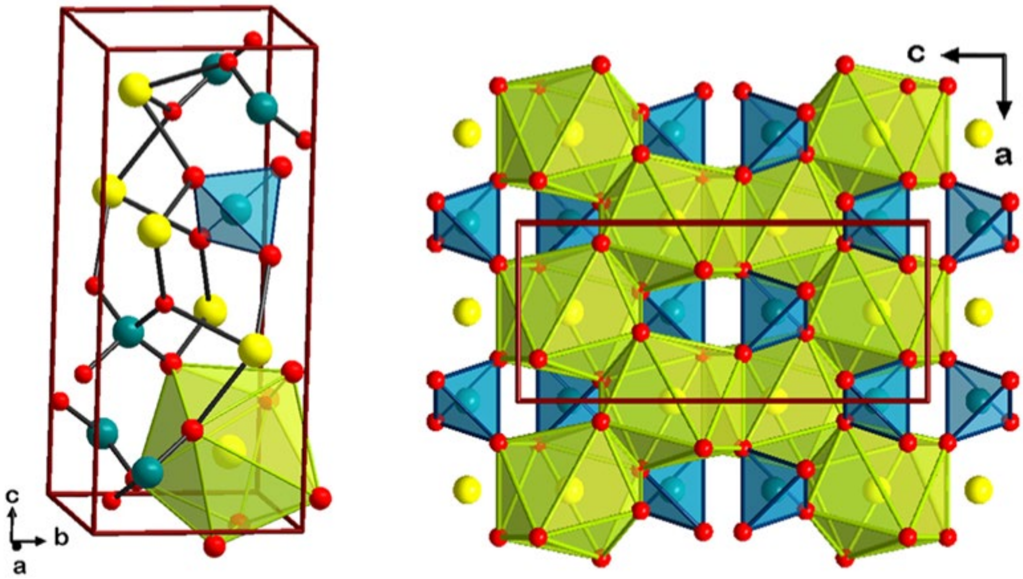

Figure 24 Representations of the scheelite-like $BaMoO_4$ structure with blue MoO_4 tetrahedra and green BaO_8 coordination polyhedra. The unit cell is drawn as brown lines. Yellow balls for Ba, red for O, and blue for Mo [83]. Reproduced with permission from ref 83. Copyright 2022, Elsevier Ltd.

In Figure 24, the scheelite-type structure of $BaMoO_4$ is illustrated with blue MoO_4 tetrahedra and green BaO_8 coordination polyhedra. Each MoO_4 unit consists of a central molybdenum atom (blue) coordinated by four oxygen atoms (red), forming a tetrahedral geometry. The following section reviews recent studies that have investigated the application of scheelite-type $BaMoO_4$ in energy storage systems, particularly as a key component in supercapacitor electrodes.

8.1 Addition of Ag/$BaMoO_4$ Nanoparticles on Recycled Tetrapak for Efficient and Flexible Solid-State Supercapacitors

Tetrapak, composed of cellulose, aluminum, and plastic, presents a promising and sustainable option for energy storage applications due to its abundance and favorable composition [84]. The incorporation of Ag/$BaMoO_4$ nanoparticles as an electrode material for supercapacitor

(SC) applications has demonstrated (Figure 25) significant potential in enhancing electrochemical performance with a maximum capacitance and energy density of 440 F/g, and 170 Wh/Kg, respectively. These nanoparticles contribute to improved charge storage capacity through surface redox reactions. This study [84] highlights the feasibility of utilizing Ag/$BaMoO_4$ nanoparticles in combination with recycled Tetrapak/graphene to fabricate efficient, flexible, and environmentally friendly supercapacitors. Notably, the addition of $BaMoO_4$ nanoparticles markedly enhanced the capacitance, energy density, and cycling stability of the SCs [84].

While the review on this material is based on a single literature [84], its significance lies in showcasing how $BaMoO_4$ can be functionalized with conductive metals and supported on eco-friendly substrates, aligning with broader trends in supercapacitor research. These trends emphasize the development of environmentally conscious materials, flexible device architectures, and doped or heterostructured $BaMoO_4$ composites to address inherent conductivity limitations. To fully contextualize the performance of Ag/$BaMoO_4$ systems, benchmarking against other metal-doped molybdates or hybrid oxide/carbon composites is essential. Such comparative studies would provide a more comprehensive understanding of the potential of $BaMoO_4$-based materials within the broader landscape of advanced supercapacitor electrodes. However, to the best of our knowledge, the articles directly related to the $BaMoO_4$ composite are scarce. Consequently, the review of dopant additions to $BaMoO_4$ is limited.

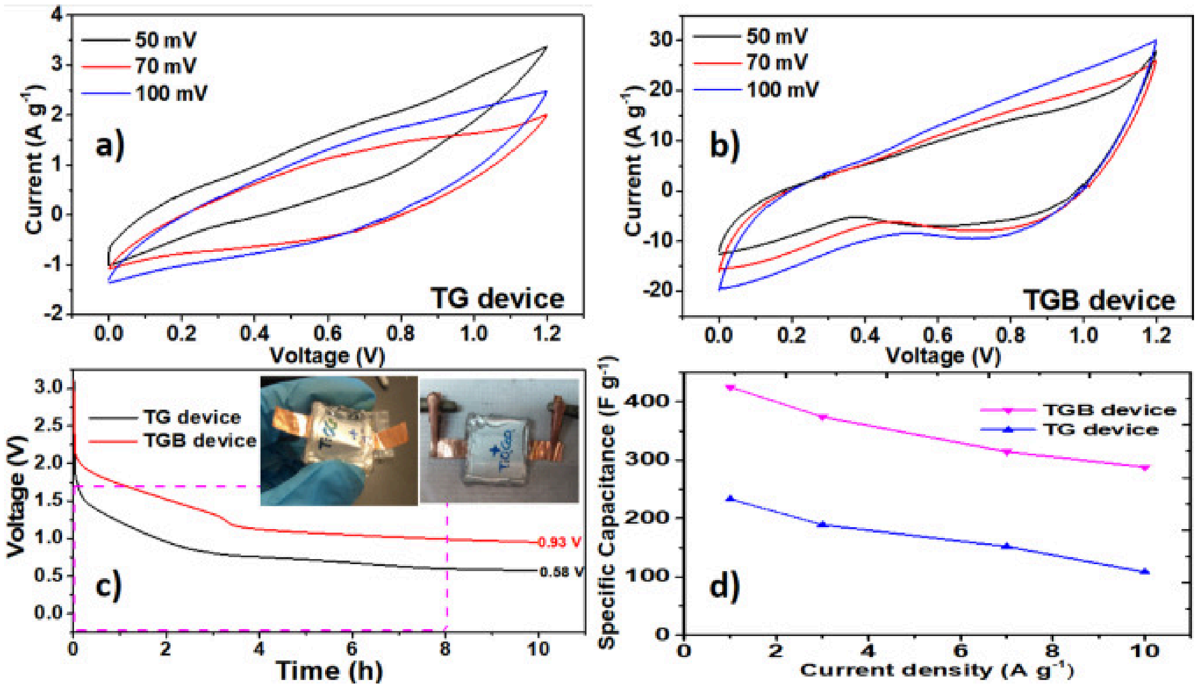

Figure 25 Cyclic voltammetry curves for the recycled tetrapak and Ag/$BaMoO_4$ nanoparticles (a) tetrapak/graphene (TG), (b) TG electrode coated with a layer of $BaMoO_4$ by using the Dr. Blade technique (TGB), (c) discharge curves for the stated electrodes, and (d) specific capacitance as a function of current density [84]. Reproduced with permission from ref 84. Copyright 2022, Elsevier Ltd.

8.1.1 Limitations & Future Prospects

Despite the encouraging electrochemical performance of the Ag/$BaMoO_4$-tetrapak system, several technical challenges must be addressed to advance its commercial viability and integration into next-generation energy storage systems, as discussed below.

Current Limitations

- ✓ **Interface Optimization and Charge Transport:** The heterojunction between Ag/$BaMoO_4$ nanoparticles and the graphene-coated cellulose substrate still restricts efficient electron transfer and interfacial adhesion. Imperfect bonding causes partial charge trapping and increased internal resistance, reducing overall conductivity and energy efficiency.

- ✓ **Scalability and Reproducibility:** While the current microwave-hydrothermal synthesis produces high-quality nanostructures at the laboratory scale, it presents reproducibility issues when scaled up. Uneven heating, local concentration gradients, and limited control over particle size distribution may affect consistency across larger batches.
- ✓ **Intrinsic Redox Limitations:** $BaMoO_4$ possesses a relatively wide band gap and limited intrinsic redox activity, which constrains energy density. The material's charge-storage capacity is primarily surface-dominated, leading to slower kinetics and lower utilization of active sites during prolonged cycling.
- ✓ **Mechanical and Environmental Stability:** Although the electrode retains over 92 % of its capacitance after 500 cycles, its long-term durability under mechanical stress, temperature fluctuation, and humidity remains unverified. Prolonged bending or environmental exposure could cause structural delamination or performance decay.
- ✓ **Integration Challenges with Other Functional Oxides:** Incorporating secondary oxide phases such as ZnO or other semiconductors has shown benefits in conductivity and stability; however, achieving uniform dispersion and stable interfaces remains difficult. Interfacial mismatch and lattice strain may result in microcracking or phase segregation over extended operation.
- ✓ **Device Architecture and Electrolyte Compatibility:** The present symmetric device configuration and acidic PVA/H_3PO_4 gel electrolyte limit the operational voltage and long-term stability. Acidic environments can promote corrosion, while the narrow voltage window restricts energy output.
- ✓ **Limited Mechanistic Understanding:** A lack of in-depth mechanistic insight into charge-transfer dynamics, ion diffusion pathways, and surface redox reactions hampers precise material design. The absence of comprehensive in-situ analyses leaves the

relationship between structure, chemistry, and electrochemical behaviour insufficiently understood.

Future Scope

Therefore, the Ag/$BaMoO_4$-tetrapak system exemplifies a new generation of eco-conscious supercapacitors, uniting the durability of BMOs with the redox versatility of BTMOs. Looking ahead, future research directions could emphasize:

- ✓ **Tailored Hybrid Design and Defect Engineering:** Developing structurally engineered BTMO-BMO hybrids with controlled morphology, defect density, and optimized electronic coupling can yield superior electrochemical activity and stability.
- ✓ **Scalable Green Fabrication:** Adopting low-temperature, solvent-minimized synthesis methods compatible with recycled substrates will enhance process sustainability while enabling large-scale production of eco-friendly electrodes.
- ✓ **Carbonaceous and Polymeric Integration:** Embedding carbon-based scaffolds (graphene, CNTs) or flexible polymer binders within the electrode framework can boost conductivity, mechanical flexibility, and electrochemical durability.
- ✓ **Advanced Device Architectures:** Designing asymmetric or hybrid supercapacitor configurations can broaden the potential window, enhance energy density, and provide balanced power performance suitable for flexible and wearable electronics.
- ✓ **Lifecycle and Environmental Assessment:** Comprehensive life-cycle evaluations and environmental impact analyses are essential to ensure that the Ag/$BaMoO_4$-Tetrapak system aligns with circular-economy goals and sustainable material management.

8.2 Samarium (Sm) doped Barium Molybdate ($BaMoO_4$) Nanostructure Candidate for Supercapacitors

Sm-doped $BaMoO_4$ significantly enhances the electrochemical performance of pristine $BaMoO_4$ by increasing surface area, reducing charge-transfer resistance, and improving electrical conductivity. The doped material demonstrates, in Figure 26, a high specific capacitance of 135 F/g at a current density of 1 A/g, along with a low charge-transfer resistance (Rct) of 2.3 Ω.

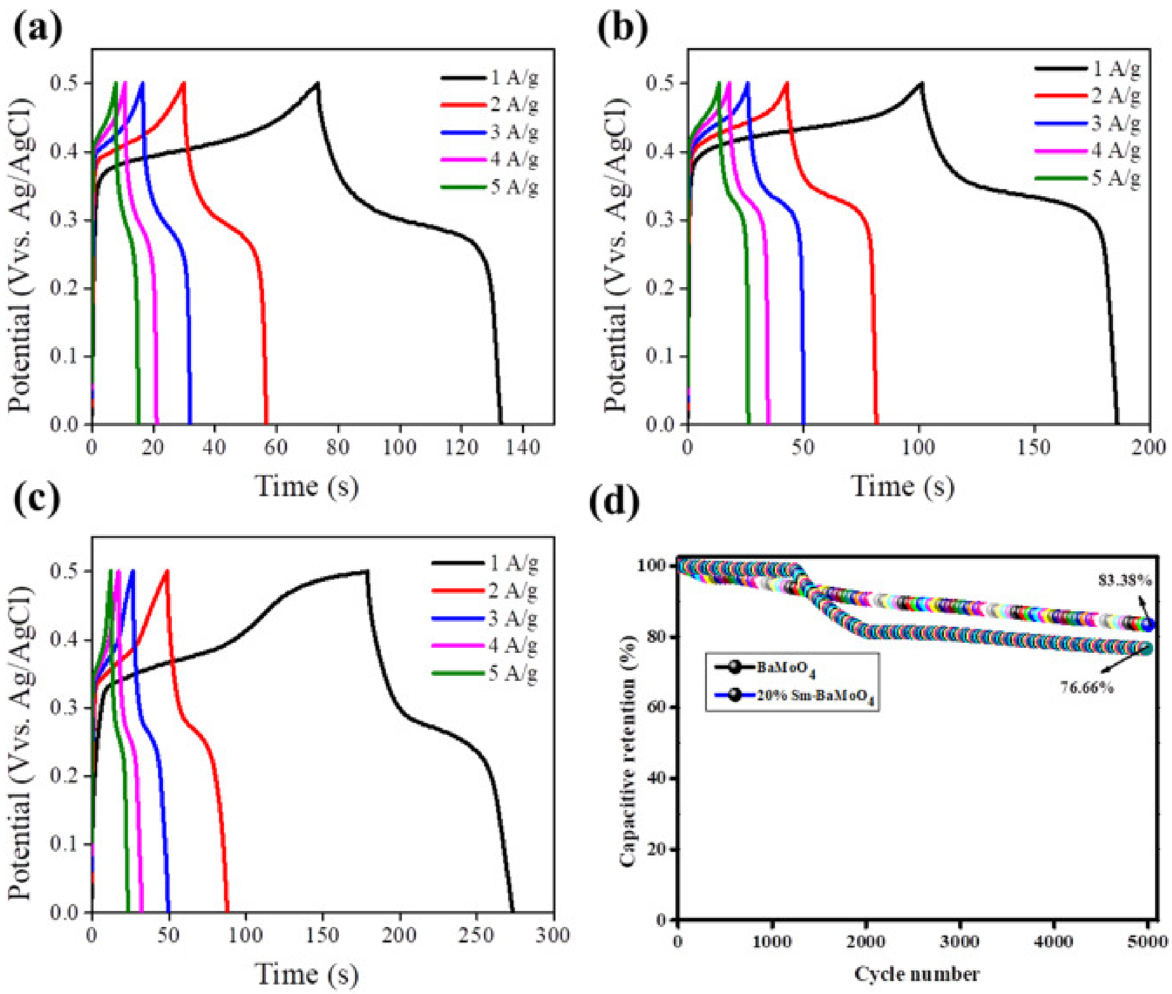

Figure 26 Charge–discharge (CD) curves for the (a) pure $BaMoO_4$ (TG), (b) 10% Sm, (c) 20% Sm doped, and (d) CD stability over 5000 cycles of Pure $BaMoO_4$ and 20 % Sm doped $BaMoO_4$ at 5 A/g. [68]. Reproduced with permission from ref 68. Copyright 2022, Elsevier Ltd.

The improved performance is attributed to the presence of multiple redox couples, Ba^{2+}/Ba^{+}, Mo^{6+}/Mo^{5+}, and Sm^{3+}/Sm^{2+}, which facilitate efficient charge storage and transfer. Notably, a 20% Sm-doped $BaMoO_4$ electrode exhibited excellent cycling stability, retaining 83.38% of its initial capacitance after 5000 charge–discharge cycles [68].

8.2.1 Limitations & Future Prospects

Although $BaMoO_4$ exhibits high power density, its energy density remains relatively low compared to other advanced materials. While Sm doping enhances its specific capacitance, the values still fall short of those reported for some recently developed electrode materials, indicating potential for further optimization. To address these limitations, integrating $BaMoO_4$ with carbon-based materials, such as graphene or carbon nanotubes, can significantly enhance surface area, electrical conductivity, and overall capacitive performance. Additionally, incorporating $BaMoO_4$ into hybrid supercapacitor systems offers a promising strategy to balance energy and power densities, thereby improving its competitiveness for practical energy storage applications [68].

8.3 BaMoO4/ZnO as Electrode Materials for Hydrogen Storage

In addition to its role in supercapacitor applications, $BaMoO_4$ has also been investigated in composite form with ZnO for hydrogen storage devices. One reported study [9] demonstrated the synergistic effect of coupling $BaMoO_4$ with ZnO, wherein ZnO contributes enhanced electrical conductivity and facilitates hydrogen adsorption. This integration led to measurable improvements in hydrogen storage capacity, highlighting the potential of $BaMoO_4$/ZnO composites in multifunctional energy systems. Traditional hydrogen storage methods, such as high-pressure gas, cryogenic liquid, and solid-state storage, face significant limitations, including safety risks and low energy efficiency. In contrast, solid-state hydrogen storage using nanocomposites has emerged as a promising alternative, offering advantages like higher storage capacity, reduced costs, and enhanced safety. Among these, transition metal oxides such as $BaMoO_4$/ZnO are particularly attractive for electrochemical hydrogen storage (EHS) due to their favourable structural and electrochemical characteristics, including high surface area, good conductivity, and strong reactivity. However, their electrochemical capacity remains a limiting factor, prompting the integration of carbon-based materials like graphene oxide (GO) and graphene quantum dots (GQDs) to boost performance [9].

Compared to other hydrogen storage materials, such as metal-organic frameworks, carbon nanotubes, and various transition metal oxides, $BaMoO_4/ZnO$ nanocomposites, particularly when integrated with carbon-based additives, exhibit superior electrochemical performance. After 15 charge–discharge cycles, as shown in Figure 27, the nanostructured $BaMoO_4/ZnO$ electrode exhibited a hydrogen capacitance of approximately 129 $mAh{\cdot}g^{-1}$. Remarkably, the incorporation of graphene-based materials significantly enhanced this performance. The $BaMoO_4/ZnO$-GQDs (graphene quantum dots) and $BaMoO_4/ZnO$-GO (graphene oxide) nanocomposites achieved maximum capacitances of 284 $mAh{\cdot}g^{-1}$ and 213 $mAh{\cdot}g^{-1}$, respectively. This substantially surpasses the pristine $BaMoO_4/ZnO$ structure. These improvements are attributed to the synergistic interaction between $BaMoO_4$ and ZnO, further amplified by the high conductivity, large surface area, and structural advantages provided by GO and GQDs. These nanocomposites were reported for hydrogen storage, and a hydrothermal synthesis has been employed to produce the binary metal oxide.

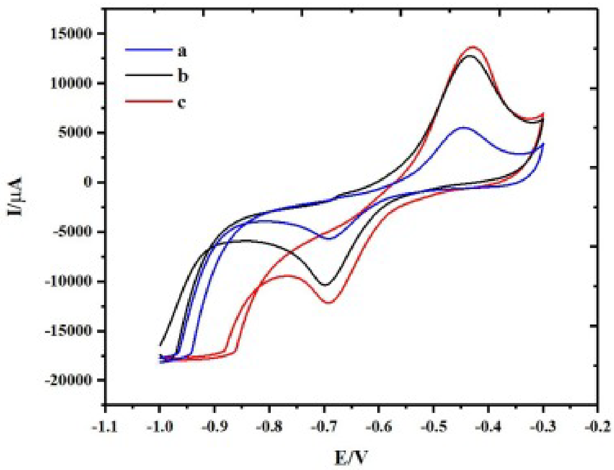

Figure 27 Cyclic voltammetry curves for (a) $BaMoO_4/Zn$), (b) $BaMoO_4/ZnO$-GO, and (c) $BaMoO_4$ ZnO-GQDs. [9]. Reproduced with permission from ref 9. Copyright 2022, Elsevier Ltd.

8.3.1 *Limitations and Future Prospects*

Although $BaMoO_4/ZnO$ nanocomposites have demonstrated significant promise for hydrogen storage and electrochemical energy applications, several inherent limitations still restrict their performance compared with typical Binary Transition Metal Oxides (BTMOs). These challenges are primarily rooted in the fundamental differences between BTMOs and Binary Metal Oxides (BMOs). Understanding and levelling these complementary characteristics is therefore critical to advancing $BaMoO_4$-based systems.

Current Limitations

- ✓ **Scalability of Synthesis:** The sonochemical method, while effective for producing nanoscale composites, is energy-intensive and difficult to scale. Industrial deployment requires alternative synthesis routes such as sol-gel, spray pyrolysis, or continuous-flow hydrothermal methods to ensure reproducibility and cost-effectiveness.
- ✓ **Surface Area Constraints:** Although GO and GQDs improved surface area (124 m^2 g^{-1} for $BaMoO_4/ZnO$-GO vs. 9.1 m^2 g^{-1} for $BaMoO_4/ZnO$), the values remain modest compared to advanced porous carbons or MOF-derived structures. Further optimization of porosity and morphology is needed to maximize ion accessibility.
- ✓ **Electrochemical Stability**: The reported cycling stability was limited to 15 cycles in hydrogen storage tests. Long-term durability under extended cycling (>1000 cycles) and varying environmental conditions remains unexplored.
- ✓ **Mechanistic Understanding:** While Mo^{6+}/Mo^{5+} redox transitions were identified as key contributors, the detailed charge-transfer pathways between $BaMoO_4$, ZnO, and carbonaceous additives require further clarification through in-situ spectroscopy and computational modelling.

Future Scope

Future research on $BaMoO_4$/ZnO-based BMOs should draw on the design principles of high-performing BTMOs to bridge the gap between conductivity and stability. This can be achieved through the following strategic directions:

- ✓ **Electronic and Structural Modulation through Doping:** Aliovalent cation doping (e.g., Ni^{2+}, Co^{2+}, Fe^{3+}) within the $BaMoO_4$ lattice can introduce intermediate redox states, analogous to those in BTMOs, thereby enhancing charge-transfer kinetics and electrochemical responsiveness. Controlled defect engineering and oxygen vacancy creation could further improve electron mobility without compromising lattice integrity. Such modifications will allow BMOs to emulate the rich redox behaviour typical of transition metal-based systems.
- ✓ **Hybridization and Interface Engineering:** Developing composite frameworks that integrate BMOs with conductive substrates such as MXenes, rGO, or carbon nanotubes can overcome the inherent electronic limitations of $BaMoO_4$. By forming heterojunctions with ZnO or other semiconductors, interfacial charge polarization can be leveraged to accelerate ion diffusion and promote faradaic reactions. These hybrid nanostructures are expected to combine the redox flexibility of BTMOs with the chemical stability of BMOs, enabling higher energy and power densities.
- ✓ **Morphological Control and Scalable Synthesis:** Future synthesis strategies should emphasize morphology control, such as constructing nanosheets, porous spheres, or core-shell architectures to optimize surface area and shorten ion-diffusion paths. Scalable methods like hydrothermal, microwave synthesis or spray pyrolysis may ensure reproducibility while reducing synthesis costs and environmental impact. Such structural refinement will be crucial to translate laboratory-scale advantages into industrially viable electrode materials.

- ✓ **Device-Level Validation and Long-Term Stability:** To realize practical benefits, $BaMoO_4$/ZnO-based electrodes must be evaluated at realistic loadings (≥ 10 mg cm^{-2}) and in full-cell configurations. Comparative studies against BTMO-based electrodes can provide quantitative insight into rate capability, voltage stability, and lifecycle performance. Employing in situ characterization techniques such as operando XRD, EIS, and Raman spectroscopy will also help elucidate reaction mechanisms, structural evolution, and degradation pathways during repeated hydrogen adsorption-desorption cycles.

9 Role of ZnO doping in enhancing $BaMoO_4$ electrodes for electrochemical energy storage

Doping ZnO into hydrogen storage materials has proven to be an effective strategy for enhancing the electrochemical performance of supercapacitor electrodes. In this review, this approach was adopted to improve the electrochemical properties of $BaMoO_4$-based composites. ZnO offers several advantageous characteristics, including excellent chemical stability, high theoretical specific capacitance, and strong electron mobility [9, 85]. These properties contribute to enhanced charge transfer kinetics and structural integrity when ZnO is integrated with other metal oxides.

In binary composites, ZnO functions as both a conductive and stabilizing phase [76]. It facilitates faster electron transport and mitigates volume changes during charge–discharge cycles, thereby improving cyclic stability. Additionally, ZnO doping introduces extra active sites for redox reactions and creates a synergistic interaction with the primary metal oxide. This leads to improved specific capacitance, better rate capability, and extended operational life [9, 85-86].

Specifically, doping ZnO into $BaMoO_4$ offers a strategic synergy that enhances key properties critical for high-performance supercapacitors. ZnO contributes high chemical stability, environmental friendliness, good ionic conductivity, and a moderate bandgap (~3.3 eV), along with a strong capacity to generate oxygen vacancies. These features help overcome $BaMoO_4$'s intrinsic limitations, such as its wide bandgap and low conductivity. ZnO also enhances pseudocapacitive charge storage by introducing additional redox-active sites and supports high surface area nanostructures that facilitate rapid ion diffusion, essential for high-rate performance. Moreover, ZnO's structural robustness ensures long-term durability during repetitive redox cycling [9]. As shown in Table 2, the ZnO-doped $BaMoO_4$ material, tested in a 2 M Na_2SO_4 electrolyte at a scan rate of 1 mV/s, exhibits a specific capacitance of 270 F/g and retains 98% of its initial capacitance after 1000 cycles [82]. This performance is superior compared to other BMO-based electrodes listed in the table. The enhanced electrochemical behavior can be attributed to the incorporation of ZnO as a dopant, which improves electrical conductivity and facilitates more efficient charge storage in the $BaMoO_4$ matrix.

ZnO is also attractive due to its abundance, low cost, and minimal environmental impact. It crystallizes in the wurtzite structure, with a wide bandgap (~3.7 eV), strong exciton binding energy (60 meV), and notable piezoelectric properties [85]. These attributes make ZnO not only a valuable dopant but also a multifunctional component in composite electrode materials. Therefore, $BaMoO_4$ doped with ZnO presents a compelling alternative for next-generation supercapacitor electrodes, particularly in flexible, solid-state, and hybrid energy storage systems.

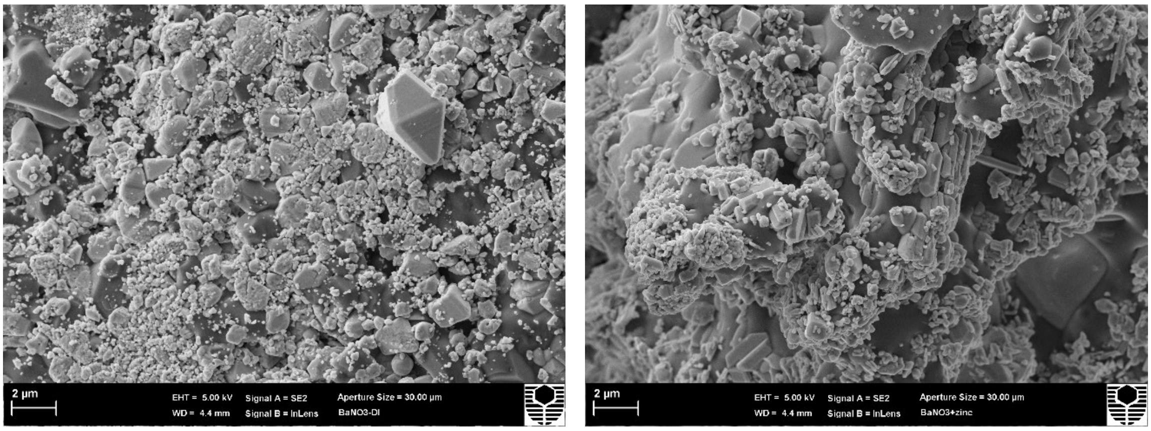

Figure 28 SEM images for scheelite-type pristine $BaMoO_4$ (left); and in the presence of Zn-doped $BaMoO_4$ (right). A distinct tetrahedral-shaped particle is visible for pristine $BaMoO_4$.

Figure 28 presents a comparative analysis of SEM images for pristine $BaMoO_4$ and Zn-doped $BaMoO_4$. A distinct morphological contrast is observed upon Zn doping. The pristine $BaMoO_4$ exhibits a well-defined scheelite-type structure, with clear evidence of Mo tetrahedral coordination. In contrast, the Zn-doped $BaMoO_4$ displays a porous morphology, lacking the distinct tetrahedral features seen in the undoped sample [82]. Although the particle sizes remain comparable between the two samples, the morphological transformation induced by Zn incorporation suggests a potential enhancement in electrochemical performance. The increased porosity and altered surface structure in the doped sample may facilitate improved ion diffusion and charge storage, making it a promising candidate for energy storage applications.

10 Challenges and Future Prospects of $BaMoO_4$/ZnO for Supercapacitors

The primary challenges of using $BaMoO_4$ material in supercapacitors includes structural degradation during repeated charge-discharge cycles, which compromises cycling stability and reduces lifespan. Additionally, the inherently low electrical conductivity of barium molybdate limits charge transport and overall rate performance. Balancing high energy and power densities, commonly referred to as the energy–power trade-off, remains a significant hurdle.

Furthermore, current synthesis methods for $BaMoO_4$ are often unsuitable for large-scale production, highlighting the need for alternative, scalable approaches to fabricate high-quality nanostructures.

To overcome these challenges, the prospects for $BaMoO_4$ doped with ZnO nanocomposites are promising and pave the pathway for improved energy storage properties. Hybrid composites, particularly those integrating carbon-based materials, can significantly enhance conductivity and electrochemical performance. Doping strategies and defect engineering can further improve redox activity by enabling access to multiple oxidation states of molybdenum. With the development of green, scalable synthesis methods using environmentally friendly precursors, $BaMoO_4$/ZnO composites hold strong potential for application in flexible and solid-state supercapacitors, as well as in hybrid systems for sustainable energy storage.

11 Conclusion and Outlook

The transition to sustainable energy systems necessitates the development of advanced, efficient, and scalable energy storage solutions. Among the various technologies, electrochemical energy storage stands out for its flexibility, portability, and high energy performance. Supercapacitors, in particular, are highly promising due to their long cycle life, high power density, and rapid charge–discharge capabilities. However, their performance is largely determined by the nature and quality of the electrode materials.

Electrochemical capacitors are poised to play an increasingly vital role in sustainable energy systems, owing to their rapid power delivery, long cycle life, and inherent safety. Within this domain, binary transition-metal oxides (BTMOs) and binary metal oxides (BMOs) offer a complementary materials platform for pseudocapacitive energy storage, enabled by accessible redox couples and tunable properties through nanostructuring, defect engineering, and hybridization with conductive frameworks. These strategies collectively help bridge the performance gap between electric double-layer capacitors and battery-type devices. Despite these advances, several bottlenecks persist, including limited intrinsic conductivity, structural instability during cycling, and performance degradation when scaling from thin electrodes to commercially relevant (thick) electrode mass loadings for practical applications. BMOs, particularly those with scheelite-type structures, present unique advantages such as low thermal conductivity and customizable electrochemical behavior via A- and B-site substitution.

Among BMOs, ABO_4 scheelites, especially $BaMoO_4$, emerge as promising candidates for aqueous systems. When paired with ZnO or other conductive dopants, $BaMoO_4$-based nanocomposites exhibit enhanced electronic transport, mechanical resilience, and interfacial kinetics. In such hybrids, the oxide contributes redox-active sites while the conductive phase facilitates efficient charge transport and short diffusion paths, addressing key challenges like low energy density and cycling fade, provided that porosity, thickness, and resistance are optimized for device-level integration.

Future progress depends on translating promising half-cell results into robust device performance. Key priorities include: (i) scalable synthesis routes that yield hierarchical porosity, controlled grain size, and reproducible defect profiles; (ii) advanced interface engineering in oxide–carbon or oxide–MXene networks to mitigate polarization at high areal loadings; (iii) electrolyte optimization across aqueous, organic, and ionic systems to balance safety, voltage window, and rate capability; and (iv) rigorous benchmarking using areal capacitance metrics, high-mass-loading rates, and long-term cycling stability.

For $BaMoO_4$/ZnO and related composites, operando diagnostics should be employed to elucidate redox mechanisms and degradation pathways, while techno-economic and life-cycle assessments guide material selection and process scalability. Addressing these challenges will enable oxide-based hybrid supercapacitors to deliver scalable, cost-effective energy storage solutions for renewable integration, grid stabilization, and electric mobility, advancing the global transition toward sustainable energy systems.

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