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CHAPTER 18

Nanostructured Metal Oxides for Supercapacitors: Computational Insights and Future Prospects

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Abstract: Nanostructured metal oxides (NMOs) have emerged as promising candidates for high-performance supercapacitors owing to their rich redox activity, high surface area, and structural versatility. This chapter provides a computationally guided overview of NMOs for supercapacitor applications, emphasizing how Density Functional Theory (DFT) and complementary theoretical tools accelerate material discovery and optimization. We systematically explore three core computational

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approaches band structure and DOS analysis, adsorption energy calculations, and surface diffusion barrier estimations via the Nudged Elastic Band (NEB) method to reveal their predictive value in tuning conductivity, ion surface interactions, and charge transport properties. Case studies demonstrate that NMOs such as $NiCo_2O_4$ achieve specific capacitances exceeding 900 F g^{-1}, while $NiMoO_4$ delivers 168.9 mAh g^{-1} with 80% retention after 7000 cycles. DFT calculations closely match experimental results for $NiMoO_4$ [110] (predicted 203 mAh g^{-1}), validating computational accuracy. Band structure and DOS analysis highlights the role of high DOS near the Fermi level in enhancing conductivity, with sulfide analogues (e.g., Co_3S_4, $NiCo_2S_4$) outperforming oxides due to reduced band gaps. Adsorption energy studies reveal optimal ion binding sites and the influence of defects, dopants, and surface terminations on stability and capacitance. NEB-based diffusion studies quantify migration barriers, showing that vacancy engineering and morphology control can significantly enhance ion mobility. This chapter concludes that the synergy between nanostructure engineering and computational modeling provides a robust pathway toward the development of commercially viable, scalable, and sustainable supercapacitors.

Keywords: Nanostructured metal oxides, Supercapacitors, Density Functional Theory, Pseudocapacitance, Computational Modeling.

1. Introduction

Global energy challenges demand efficient, sustainable, and high-performance energy storage solutions. While batteries dominate in high-energy applications, supercapacitors are unparalleled in applications requiring high power density, rapid charge–discharge rates, and exceptional cycling stability [1,2]. These advantages make supercapacitors crucial in electric vehicles, backup power systems, and portable electronics. Among various electrode materials, NMOs have emerged as key players due to their tunable redox properties, high surface area, and morphology-dependent electrochemical performance [3]. NMOs contribute significantly to pseudocapacitive behavior, where fast and reversible Faradaic reactions complement electric double-layer capacitance, resulting in higher energy storage capability. This chapter focuses on the role of NMOs in supercapacitors, highlighting how computational methods particularly DFT advance our understanding of their properties and guide the design of next-generation electrodes. The motivation for this chapter arises from the need to accelerate the development of high-performance supercapacitor materials while reducing experimental costs and time. Computational modeling, especially DFT, provides a powerful framework to predict the structural, electronic, and electrochemical properties of NMOs at the atomic level before synthesis, thereby guiding targeted experimental investigations [4,5]. DFT enables the study of critical parameters such as band structure, DOS, adsorption energies, surface diffusion barriers, and charge distribution, all of which directly influence capacitance, rate capability, and cycling stability [6–8]. These insights are particularly valuable for materials containing transition metals, where strong electron correlations require advanced computational approaches like Hubbard-U correction (DFT+U) or hybrid functionals to accurately capture localized electronic states [9].

This chapter is structured into interconnected sections. The section Theoretical Calculations for Supercapacitors: A DFT Perspective provides the fundamental principles of DFT and explains its relevance in probing ion–surface interactions, electronic structures, and charge storage mechanisms [10]. The section Band Structure and DOS Calculations emphasizes how the electronic band gap and DOS near the Fermi level determine electronic conductivity and redox behavior, with examples showing why metal oxides, such as $NiCo_2O_4$ and Co_3O_4, shows pseudocapacitive behavior[11]. In Adsorption Energy Calculations, the focus shifts to quantifying ion adsorption strengths and identifying preferred adsorption sites (top, bridge, hollow), with case studies on Li^+, Na^+, K^+, OH^-, and H^+ adsorption on metal oxides and sulfides. The section Surface Diffusion Barrier Calculations applies the NEB method to determine ion migration pathways and activation energies, highlighting how structural features such as vacancies, defects, and dopants can lower diffusion barriers and enhance rate performance [12]. Additionally, Other Computational Approaches such as Molecular Dynamics (MD), Finite Element Analysis (FEA), and Machine Learning are briefly introduced to illustrate their complementary role in predicting thermal stability, mechanical robustness, and accelerating material discovery [4,13],14 This chapter will be particularly useful for materials scientists, electrochemists, and computational researchers working on energy storage technologies. Graduate students and early-career researchers will benefit from the clear explanations of DFT methodologies applied to supercapacitors, while industrial research and development teams can use the insights to streamline material screening and design processes. By combining nanostructure engineering with computational modeling, this chapter offers a roadmap for developing NMOs with optimized conductivity, stability, and electrochemical performance, thereby contributing to the advancement of next-generation supercapacitors.

2. Types of Supercapacitors and Role of Metal Oxides

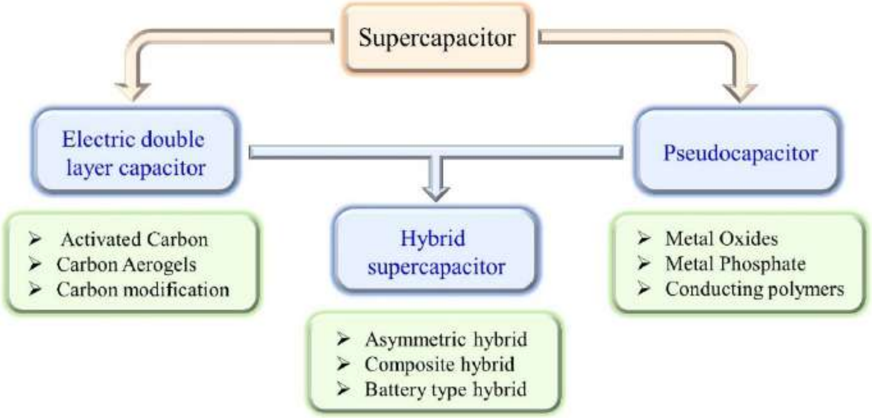

Fig. 1. Classification and schematic illustration of supercapacitor.

Supercapacitors are unique energy storage devices that stand between conventional capacitors and rechargeable batteries in terms of power and energy density. Their classification is primarily based on how they store charge, which in turn depends on the interactions between the electrode materials and the

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electrolyte. Broadly, they can be divided into three major categories: electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors [15]. The classification and schematic illustration of supercapacitors are shown in Fig. 1.

2.1 Electrochemical Double-Layer Capacitors

In EDLCs, charge storage occurs electrostatically, without any actual transfer of electrons or ions across the electrode-electrolyte interface. Instead, when a potential is applied, positive and negative ions in the electrolyte rearrange themselves on the surface of the oppositely charged electrodes, forming what is known as the electric double layer [15–17]. This is a purely non-Faradaic process meaning no chemical bonds are broken or formed and therefore, the electrode structure remains unchanged during cycling. The result is an exceptionally long cycle life, often exceeding hundreds of thousands of cycles. The amount of charge stored is directly linked to the accessible surface area of the electrode and the distance between the charge layers. Carbon-based materials such as activated carbons, carbon nanotubes, and graphene are ideally suited for EDLCs due to their very high surface area, good electrical conductivity, and chemical stability [18]. Fig. 2(A-C) compares the cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) profiles for an EDLC. The CV curve displays a nearly perfect rectangular shape, characteristic of ideal capacitive behavior arising from electrostatic charge storage at the electrode–electrolyte interface. The corresponding potential–time plot is linear during both charging and discharging, reflecting the constant current response typical of EDLCs.

Biomass-derived and nanostructured materials have demonstrated outstanding potential as electrode candidates for high-performance supercapacitors, with each system offering unique advantages in capacitance, rate capability, and cycling stability. Tea-waste-derived porous carbon, prepared via pre-carbonization, acid washing, and optimized KOH activation (1:2 TWC/KOH ratio at 700 °C for 1.5 h), exhibited a large specific surface area of 1610 $m^2\ g^{-1}$ and a hierarchical porous structure, enabling efficient ion transport and high electroactive surface accessibility[19]. Electrochemical testing in 6 M KOH using a three-electrode configuration revealed a high specific capacitance of 332 $F\ g^{-1}$ at 1 $A\ g^{-1}$ and 222 $F\ g^{-1}$ at 100 $A\ g^{-1}$, indicating excellent rate performance even with a 100-fold increase in current density, along with remarkable cycling stability, retaining 97.8 % of its initial capacitance after 100,000 cycles. Similarly, peanut-shell-derived porous carbon prepared through hydrothermal treatment, $ZnCl_2$ activation, and pyrolysis achieved a high surface area of 1549 $m^2\ g^{-1}$ and delivered a specific capacitance of 333 $F\ g^{-1}$ at 0.5 $A\ g^{-1}$, while maintaining 54.7 % capacitance retention from 0.25 to 50 $A\ g^{-1}$ and exhibiting only 4.7 % loss after 10,000 cycles, confirming its excellent rate capability and stability [20]. Beyond carbon-based EDLC electrodes, a surfactant-assisted hydrothermal approach for $ZnCo_2O_4$ nano-hexagons using polyvinylpyrrolidone and cetyltrimethylammonium bromide yielded a remarkable specific capacitance of 2515 $F\ g^{-1}$ at 1 $A\ g^{-1}$ in 1 M Na_2SO_4, with 96 % capacitance retention after 10,000 cycles [21]. When assembled into an asymmetric $ZnCo_2O_4$//AC device, the system delivered an impressive energy density of 90 $Wh\ kg^{-1}$ at a power density of 800 $W\ kg^{-1}$, retaining 94 % capacitance over 10,000 cycles. Collectively, these results demonstrate that through appropriate material design whether biomass-derived porous carbon or nanostructured transition metal oxides it is possible to achieve a balance of high capacitance, superior rate capability, and long-term durability, meeting the performance requirements for next-generation supercapacitor applications [19–21].

2.2 Pseudocapacitors

Unlike EDLCs, pseudocapacitors store energy through fast and reversible Faradaic reactions occurring at or near the surface of the electrode material. This involves charge transfer between the electrode and the electrolyte, often through redox reactions, intercalation of ions, or electrosorption processes[15,18,22,23]. Because these reactions actively involve the electrode material, pseudocapacitors generally achieve much higher specific capacitance and energy density than EDLCs, while still maintaining good power capability. Pseudocapacitance can arise in two main forms, Surface-redox (intrinsic) pseudocapacitance where the charge storage is dominated by rapid redox reactions confined to the surface or near-surface of the electrode. Transition metal oxides such as RuO_2, MnO_2, Fe_3O_4, and NiO are well-known examples due to their multiple oxidation states, which facilitate fast electron and ion transfer[18,24–26]. Conducting polymers like polyaniline and polypyrrole also exhibit intrinsic pseudocapacitance because of their redox-active backbones. In CV profiles, these materials show quasi-rectangular shapes, and in GCD curves, quasi-triangular profiles like EDLCs but with slightly noticeable redox features. And Intercalation pseudocapacitance in this type ions from the electrolyte penetrate into the bulk of layered or tunneled electrode materials (such as Nb_2O_5, TiO_2(B), and MoO_3) without causing a crystallographic phase change [18,27]. Fig. 2(D-F) compares the CV and GCD profiles for a pseudocapacitor. Unlike EDLCs, the CV curve of a pseudocapacitor exhibits broad, symmetric redox peaks, which are characteristic of Faradaic charge storage processes involving fast, reversible surface redox reactions. These peaks indicate electron transfer between the electrode material and electrolyte species. The corresponding potential–time (charge–discharge) profile is nonlinear, displaying a slight curvature rather than a perfect triangular shape. This behavior reflects the potential-dependent nature of the redox reactions, which contribute to higher specific capacitance compared to EDLCs. This is distinct from battery behavior because the intercalation occurs rapidly and reversibly, without the sluggish solid-state diffusion that typically limits battery kinetics. In CV, intercalation pseudocapacitors often show a linear dependence of current on scan rate, with minimal peak shifts, indicating fast kinetics. Pseudocapacitors offer the advantage of higher energy density compared to EDLCs, but they may suffer from limited cycling stability depending on the electrode material's structural robustness.

Recent advancements in pseudocapacitor electrode design have focused on optimizing morphology, conductivity, and interfacial chemistry to achieve high capacitance, excellent rate performance, and long cycling stability. Ni-based metal–organic frameworks (Ni–MOFs) prepared via solvothermal synthesis demonstrated a specific capacitance of 1457.7 F g^{-1}, which increased to 2192.4 F g^{-1} at 1 A g^{-1} upon hybridization with 3 wt% graphene oxide (Ni–MOFs@GO), with 85.1% retention after 3000 cycles, owing to their unique flower-like structure and strong Ni–MOF/GO synergy [28]. Oxygen-deficient tungsten oxide ($W_{18}O_{49}$) nanorods hybridized with RuO_2 exhibited a transformation from battery-type to pseudocapacitive behavior, delivering a doubled capacitance of 1126 F g^{-1} (CV) and 1050 F g^{-1}

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(GCD) with improved stability over 3000 cycles, attributed to defect engineering and enhanced conductivity [29]. An Ag-incorporated bimetallic sulfide/metal oxide heterostructure ($Ag–Co_{9-x}Fe_xS_8@\alpha–Fe_xO_\gamma$) achieved 213.6 mAh g^{-1} at 1 A g^{-1} with 93.2% retention over 20,000 cycles, while a flexible solid-state device based on this electrode delivered 259 F g^{-1} and 80.9 Wh kg^{-1}, maintaining 92.8% retention after 5000 cycles [30]. A nanoporous Ag framework decorated with Fe_2O_3 (np–Ag@Fe_2O_3) reached ∼608 F g^{-1} at 10 A g^{-1} and retained 84.9% of its capacitance after 6000 cycles, benefiting from its high surface area and conductivity [31]. Furthermore, oxygen-deficient $Fe_2O_3–\delta$ nanorod arrays with a crystalline core/amorphous shell heterostructure on graphene delivered 701 F g^{-1} at 1 A g^{-1}, nearly twice that of conventional $Fe_2O_3–\delta$, along with enhanced rate capability and durability, while a similar design for $Co_3O_4–\delta$ nanosheets yielded superior pseudocapacitive performance in flexible asymmetric devices[32].

2.3 Hybrid Supercapacitors

Hybrid supercapacitors combine the strengths of EDLCs and pseudocapacitors in a single device, using one electrode that stores charge electrostatically and another that stores it Faradaically [15,33,34]. Fig. 2(G-I) illustrates the CV and GCD profiles for a hybrid or battery-type supercapacitor. The CV curve typically shows distinct redox peaks with a more pronounced deviation from the rectangular shape observed in EDLCs, indicating slower, diffusion-controlled Faradaic reactions occurring within the bulk of the electrode material. The corresponding charge–discharge curve displays a nonlinear, plateau-like behavior similar to that seen in rechargeable batteries, reflecting the voltage dependent insertion/extraction (intercalation) of ions. This combination of double-layer capacitance and battery-like Faradaic processes allows hybrid supercapacitors to deliver higher energy density than EDLCs while maintaining better power density and cycle life than conventional batteries. This approach enables the device to operate over a wider voltage window, resulting in higher energy density while retaining much of the power density and cycling stability of EDLCs. For example, an asymmetric configuration may use activated carbon as the negative electrode and a transition metal oxide such as Ni $(OH)_2$ as the positive electrode. The combination allows simultaneous exploitation of the fast ion adsorption of EDLCs and the high-capacity redox reactions of pseudocapacitors. However, because one electrode is often battery-like, hybrid devices may experience slightly reduced cycling life compared to pure EDLCs, and careful material design such as nanoscaling the battery type electrode or integrating conductive additives like graphene is often required to maintain high-rate performance [15,18].

Hybrid supercapacitors (HSCs), which integrate battery type Faradaic electrodes with EDLC type electrodes, offer an effective balance between high energy density and power density, making them suitable for next-generation energy storage devices. A ternary composite of nickel selenide, reduced graphene oxide, and graphitic carbon nitride (NiSe/g-C_3N_4/rGO) demonstrated outstanding performance, achieving a specific capacity of 412.6 mAh g^{-1} at 1 A g^{-1}, owing to its π-conjugated layered structure that enhances electron/ion transport and provides abundant ion diffusion channels. Assembled with activated carbon as the negative electrode, the HSC device delivered 65.2 Wh kg^{-1} at 750 W kg^{-1} with 93.3% capacity retention after 10,000 cycles [35]. For NH_4^+-based HSCs, a 2D conjugated Cu–HHB MOF embedded with iodine (Cu–HHB/I_2) provided an aerial capacitance of 111.7 mF cm^{-2} at 0.4 mA cm^{-2}, leveraging high conductivity, porous structure, and Cu–O_4 active sites to stabilize polyiodide species. Paired with a porous MXene anode, the device delivered 31.5 mWh cm^{-2} and retained 89.5% capacitance after 10,000 cycles [36]. Multivalent-ion storage was exploited in aqueous zinc-ion hybrid supercapacitors (ZHSs) using MnO_2 nanorods and activated carbon. The synthesized ZHSs achieving maximum specific capacity of 54.1 mAh g^{-1} and high energy density of 34.8 Wh kg^{-1} under optimal conditions, with ultra-fast charge–discharge (2–17 s) and high-power densities of 3.3–13.0 kW kg^{-1}. Electrolyte engineering with Mn^{2+}-containing $ZnSO_4$ raised the energy density to 58.6 Wh kg^{-1}, while SO_4^{2-} to $CF_3SO_3^-$ substitution improved stability, retaining 93.4% capacity after 5000 cycles [37]. These results highlight the importance of synergistic material design, ion-storage chemistry, and electrolyte optimization for advancing HSC performance.

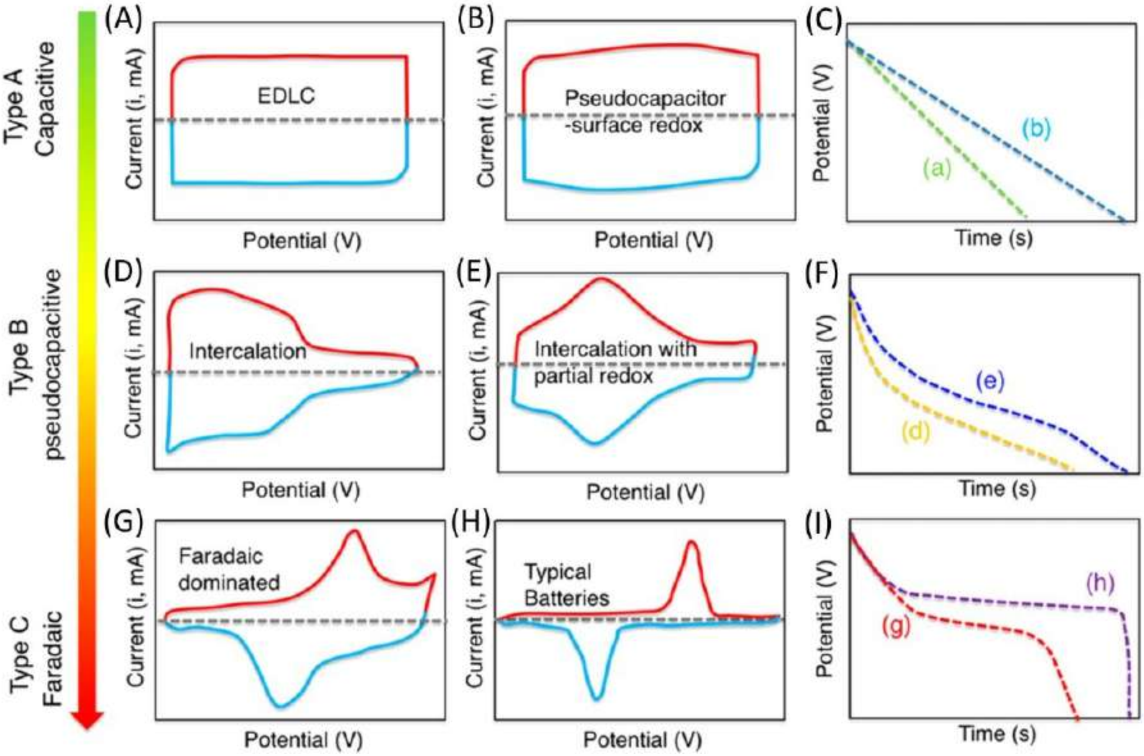

Fig. 2. Schematic representation of (A-C) electrochemical double-layer capacitors, (D-F) pseudocapacitors, and (G-I) hybrid/battery-type supercapacitors. Panels (A, D, G) show the characteristic of CV curves, while (B, E, H) depict the corresponding GCD curves profiles. EDLCs display nearly rectangular CV curves and linear, triangular charge–discharge profiles, indicative of purely electrostatic, non-Faradaic charge storage. Pseudocapacitors exhibit broad, symmetric redox peaks in CV and nonlinear charge–discharge curves, reflecting fast and reversible surface redox reactions. Hybrid/battery-type supercapacitors show pronounced redox peaks and plateau-like charge–discharge profiles, characteristic of diffusion-controlled ion intercalation processes that combine capacitive and battery-like behaviour. Reproduced from ref. [38] with permission from ACS, copyright 2018.

3. Nanostructured Metal Oxides: Properties and Potential in Supercapacitors

NMOs have emerged as vital components in the advancement of next-generation energy storage technologies due to their unique physicochemical characteristics. Their reduced dimensionality and high surface to volume ratio offer significant advantages, including enhanced surface area, tunable morphology, and superior electrochemical reactivity [39,40]. One of the abilities to control the morphology of NMOs synthesizing them in various forms such as nanoparticles, nanosheets, nanorods, and hierarchical frameworks enables optimization of other crucial properties, including electrical conductivity, porosity, and mechanical stability. Such morphological tuning plays a key role in improving the overall electrochemical behaviour and mechanical durability of energy storage devices [39,41]. Another critical advantage of nanostructuring is the enhancement of both electronic and ionic conductivity. At the nanoscale, reduced diffusion lengths and increased grain boundaries contribute to improved charge carrier mobility, which helps minimize internal resistance and improves rate performance [39,40]. Moreover, many metal oxides inherently possess multiple oxidation states, allowing them to undergo fast and reversible redox reactions. Oxides like MnO_2, Fe_2O_3, and Co_3O_4 are known for their rich redox chemistry, which contributes significantly to pseudocapacitive behaviour and high energy storage capability [40]. Metal oxide nanosheets have shown considerable promise in achieving both high power and energy density, thus outperforming traditional carbon-based supercapacitors in many cases [42]. Overall, NMOs offer a compelling combination of high surface area, tailored morphology, redox versatility, and chemical robustness, making them highly promising for advanced energy storage applications. While challenges such as structural degradation and limited electrical conductivity still exist, current research especially when integrated with theoretical modelling and green synthesis methods is rapidly addressing these limitations. The continuous development and optimization of NMOs hold immense potential for enabling scalable, efficient, and sustainable energy solutions [39,40,43].

3.1. Electronic, ionic, and redox properties of NMO’s

The ability to tune the crystal structure and morphology of NMOs plays a foundational role in enhancing their performance in energy storage devices. However, beyond just physical structuring, the electronic, ionic, and redox properties of these materials fundamentally dictate how efficiently they store and transport charge. These intrinsic properties are often tightly coupled with morphology and crystallographic orientation meaning that the benefits of morphological tuning are only fully realized when combined with an understanding of the material’s electronic structure and redox behaviour. NMOs are at the forefront of energy storage device research precisely because of this synergy between structure and intrinsic properties. Their electronic, ionic, and redox characteristics have a direct impact on their functional performance in batteries, supercapacitors, and hybrid systems. For instance, electronic conductivity in NMOs is heavily influenced by their band structure, which is in turn affected by particle size, shape, and phase. Materials like WO_3, ZnO, TiO_2, FeOx, and VO_2 exhibit tunable band gaps and electron transport properties depending on their morphology and crystallinity, allowing researchers to engineer charge mobility at the nanoscale [44,45]. Despite these tunable properties, many NMOs suffer from inherently low electronic conductivity. This challenge is commonly addressed through hybridization with conductive materials like graphene or carbon nanotubes, which substantially enhance electron mobility and electrode performance [46,47]. In addition to their electronic behaviour, NMOs often exhibit favourable ionic conductivity, especially in materials designed as mixed ionic electronic conductors, such as certain Ruddlesden-Popper oxides. These materials support fast and efficient ion transport during charge discharge cycles, making them suitable for high power applications [45,48]. Morphological tuning further complements this by increasing surface area and shortening ion diffusion paths, enabling rapid ion transport and high-rate capability in supercapacitors and lithium-ion batteries [45,49]. This close interplay between morphology and ionic conductivity illustrates why nanostructuring is such a critical design parameter. Perhaps the most defining feature of NMOs in energy storage is their redox activity [45,49].

4. Theoretical and Computational Approaches for Supercapacitor Electrodes

Energy storage devices such as batteries, supercapacitors, and hybrid systems are essential for modern energy infrastructure. Theoretical and computational methods accelerate material discovery, optimize performance, and predict long-term behavior, particularly for metal oxide electrodes. These approaches reveal charge storage, transport, and electrochemical mechanisms at the atomic level, providing fundamental insights into redox reactions, ion transport, and the relationship between electric potential and chemical energy [50]. This theoretical framework is crucial for evaluating metal oxide behavior during electrochemical cycling, while thermodynamic analysis assesses reaction feasibility and efficiency through changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), adsorption energy, quantum capacitance, etc. [51,52]. This is particularly useful for evaluating phase stability and reaction spontaneity in metal oxides, while kinetic theory examines ion diffusion, activation barriers, and charge transfer dynamics that determine power density and rate capability [53]. These theoretical tools help predict the capacity, voltage window, and stability of metal oxides and other emerging materials for energy storage [54]. Complementing theoretical insights, computational methods provide powerful tools for simulating material behavior across different length and time scales. At the quantum mechanical level, DFT is widely applied to investigate the electronic structure of metal oxides, enabling the calculation of band structures, redox potentials, ion diffusion barriers, and adsorption energies parameters crucial for optimizing electrochemical performance [4,5]. At a more dynamic scale, MD simulations capture the real time motion and interactions of ions and molecules under operational conditions, providing insights into material behavior under stress, temperature fluctuations, and repeated cycling [13]. Beyond atomistic modeling, FEA simulates mechanical deformation, thermal gradients, and electrochemical fields in device architectures, aiding in structural integrity and thermal management assessments for large scale batteries [55]. Phase field modeling further reveals microstructural evolution during cycling, including phase transformations, crack formation, and degradation pathways, thereby helping mitigate capacity fade [56]. More recently, Machine Learning and other data driven approaches have emerged as promising tools for predicting material properties, optimizing compositions, and assisting in the interpretation of complex simulation and experimental datasets [57].

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The combined application of these theoretical and computational tools offers several strategic advantages. First, they accelerate material discovery by identifying promising candidates for electrodes, electrolytes, and catalysts without resorting to time consuming and costly trial and error experimentation [57]. Second, they enable performance optimization by guiding the design of nanostructured and doped metal oxides with enhanced conductivity, high theoretical capacities, and improved cycling stability [58]. Third, they contribute to lifetime prediction and cost analysis by simulating full device operation, allowing for the assessment of environmental impact, economic viability, and mechanical robustness under realistic conditions [59]. Despite these advancements, several limitations persist that must be acknowledged. A major limitation is the high computational cost of methods like DFT, MD, and detailed FEA, which restricts their application to small systems or short time scales, reducing their practicality for complex, real world devices [60]. Furthermore, scaling limitations in MD and phase-field modeling hinder their ability to capture phenomena over the large spatial and temporal scales relevant to real-world energy storage systems, often requiring simplifications that may reduce accuracy or transferability [61]. Another major challenge is the reliance on experimental validation, as the effectiveness of theoretical predictions and computational outputs depends heavily on their correlation with empirical data. Discrepancies between simulations and experiments arising from environmental factors, material imperfections, or unaccounted physical effects can compromise reliability and necessitate ongoing calibration [62]. Additionally, DFT accuracy is constrained using approximate exchange–correlation functionals, which may inadequately predict key electronic properties such as band gaps and redox potentials, both critical for evaluating electrode material performance and stability [63]. These limitations highlight the need for a multidisciplinary approach that integrates modeling with experimental research, advances scalable and accurate simulation techniques, and fosters critical interpretation of computational results. Despite the challenges, theoretical and computational approaches remain indispensable in advancing our understanding of metal oxides in energy storage. Their continued evolution will be key to unlocking next-generation materials and architectures that meet the growing demands for safe, efficient, and sustainable energy storage technologies.

5. Theoretical Calculations for Supercapacitors: A DFT Perspective

DFT has become one of the most widely used computational tools for exploring and predicting the properties of materials at the atomic scale. At its core, DFT transforms the complex many-electron Schrödinger equation into a more manageable form by focusing on the electron density rather than the wavefunction, making it possible to model realistic systems without prohibitive computational cost [10,64]. The Born–Oppenheimer approximation further simplifies the problem by treating nuclei as stationary while solving for electronic behavior [65]. The theoretical foundation of DFT rests on the Hohenberg–Kohn theorems, which establish that the ground-state electron density uniquely determines all the properties of a system, and the Kohn–Sham formalism, which introduces a fictitious system of non-interacting electrons that reproduces the same density as the real interacting system[66] [67]. This approach enables practical and accurate calculations for a wide range of materials, including the complex transition-metal oxides often used in supercapacitor electrodes. However, because many transition-metal oxides exhibit strong electron–electron correlations, standard DFT methods sometimes fail to capture their localized electronic states accurately. To address this, improved approaches such as DFT+U and hybrid functionals (e.g., HSE06, B3LYP) are employed, providing better descriptions of electron localization and exchange–correlation effects [9]. Recent computational advances, such as efficient eigenvalue solvers like the ELSI interface, now allow DFT to handle systems with thousands of atoms, enabling realistic modeling of nanostructured electrodes and their interfaces [68]. In the field of supercapacitors, DFT offers deep insights into fundamental properties that control device performance. It can reveal the electronic band structure and DOS (which determine conductivity), quantify the adsorption energies of electrolyte ions, and map the pathways and barriers for ion migration all of which are critical for optimizing pseudocapacitance and quantum capacitance [69]. By bridging the gap between atomic-level behavior and macroscopic performance, DFT serves as a powerful guide for designing nanostructured metal oxide electrodes with enhanced energy and power density.

5.1. Band structure and density of states (electronic conductivity)

Band structure and DOS calculations are among the most powerful theoretical tools for understanding how electrode materials perform in supercapacitors. Their strength lies in revealing the fundamental link between a material's electronic structure and its ability to store and deliver charge. In simple terms, the band structure describes the distribution of electron energy levels, while the DOS quantifies how many of these electronic states are available at each energy level. A high DOS near the Fermi level is especially desirable, as it indicates a greater number of charge carriers available for conduction translating directly into higher electrical conductivity and improved charge storage capability [6],[70]. In NMOs such as $NiCo_2O_4$ and Co_3O_4, DOS and band structure calculations have shed light on why these materials display strong pseudocapacitive behavior, driven by surface redox reactions [11]. However, despite their excellent redox activity, many oxides suffer from relatively wide band gaps and a lower DOS near the Fermi level, which limit their intrinsic conductivity. Also, from the DOS and Band structure analysis it is revel that the defects in metal oxides, such as oxygen vacancies in TiO_2 and VO_2, introduce donor levels that can trigger a metal insulator transition, while in layered manganese oxides, Anti-Frenkel defects can locally enhance conductivity by orders of magnitude [6,71]. Example, defects in TiO_2 and ZnO have been linked to defect induced ferromagnetism and altered magneto-transport properties [11]. From the study of doping in ZnO the band and the DOS reveal the chang in the band gap after doping of 3% Fe and 6% Fe[72]. From another study of doping of Cu, Ag and Au in β-Ga_2O_3 shows change in the band gap from 4.853 eV to 0.982 eV as shown in Fig. 3[73]. In summary, DOS and band structure calculations serve as a bridge between fundamental quantum mechanics and practical supercapacitor performance. They reveal why certain materials like sulfides excel over oxides, show how atomic-scale modifications can tune conductivity and charge storage, and provide a rational pathway for designing next-generation nanostructured electrode materials with superior electrochemical performance.

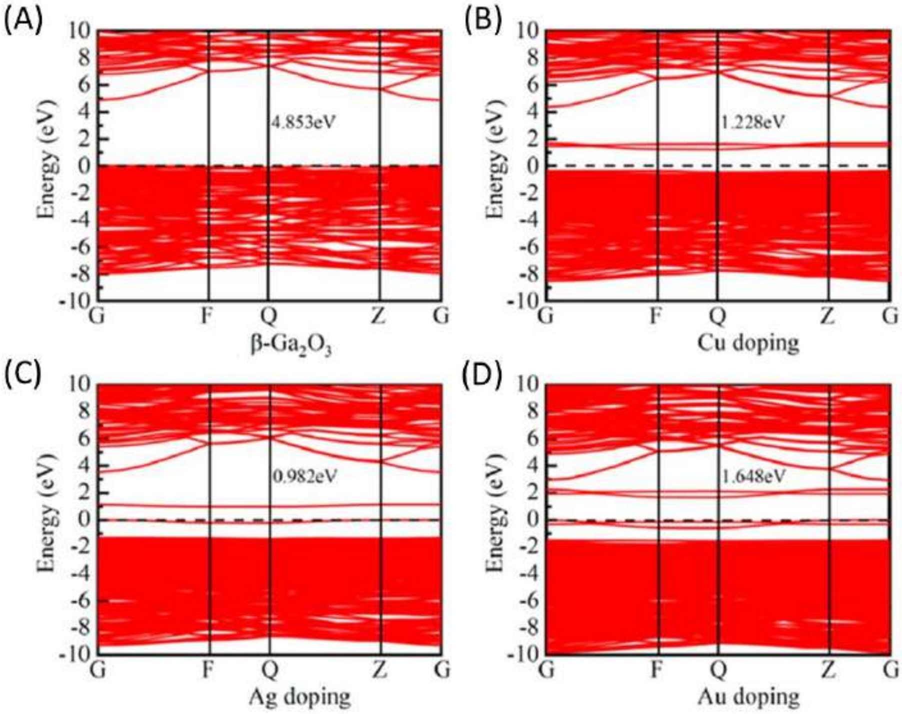

Fig. 3. (A) Band structure of β-Ga_2O_3 (B)Band structure of β-Ga_2O_3 after doping of Cu atom (C) Band structure of β-Ga_2O_3 after doping of Ag atom (D) Band structure of β-Ga_2O_3 after doping of Au atom (A-D) Reproduced from ref. [73] with permission from ACS, copyright 2025.

5.2. Adsorption energies of electrolyte ions

Adsorption processes are central to the operation of supercapacitors, as they underpin both electric double-layer formation and pseudocapacitive charge storage. In EDLCs, the accumulation of electrolyte ions at the electrode–electrolyte interface forms the double layer, a process strongly influenced by the electrode's surface area, porosity, and electronic structure [74]. Nanostructured materials with optimized morphologies can significantly enhance ion accessibility, while flat and well-ordered surfaces generally promote more uniform ion adsorption compared to highly curved surfaces[74]. Faster ion adsorption/desorption dynamics directly translate to higher power density [75]making adsorption kinetics as important as adsorption capacity. In pseudocapacitive materials, adsorption often involves partial charge transfer or redox reactions at the electrode surface, further contributing to overall capacitance. The energetics of this process can be quantified by adsorption energy calculations, which determine how strongly an ion or molecule binds to the electrode surface. The adsorption energy E_{ads} is calculated using the relationship:

$$E_{ads} = E_{total} - (E_{surface} + E_{adsorbate})$$

Where E_{total} is the total energy of the adsorbate surface system, $E_{surface}$ is the energy of the clean surface, and $E_{adsorbate}$ is the energy of the isolated adsorbate [7]. A negative E_{ads} value indicates an exothermic and thermodynamically favorable adsorption process, with larger magnitudes signifying stronger binding. In supercapacitor electrodes, strong adsorption can enhance ion anchoring, improve interfacial stability, and even introduce new active sites for redox reactions [76]. Identifying the most favorable adsorption sites is equally important. On metal oxide and sulfide surfaces, three primary configurations are typically considered: top sites (adsorbate directly above a single atom), bridge sites (between two atoms), and hollow sites (coordinated by three or more atoms). In many systems, hollow sites tend to provide the strongest adsorption due to greater coordination and electronic interaction [12]. For example, sulfur adsorption on Ir [100] preferentially occurs at the hollow site, as confirmed by its most negative adsorption energy [77]. Charge density difference analysis further clarifies the bonding nature regions of electron accumulation at the interface indicate strong polar covalent interactions. DFT studies extend this approach to explore how different ions such as Li^+, Na^+, K^+, $OH^–$, and H^+ interact with oxide and sulfide surfaces. These interactions are governed by a combination of factors: charge transfer, ionic size, coordination preference, and defect chemistry. For instance, K adsorption on TiO_2 involves electron transfer from K 3s orbitals to Ti 3d orbitals, forming K^+ and inducing surface relaxation [78], while Li adsorption on MgO [001] results in strong polarization and localized electron pairs [79]. Oxygen vacancies can significantly enhance $OH^–$ adsorption on TiO_2 [80], and H adsorption on CeO_2 is strongly influenced by electron-deficient lattice oxygen sites [81]. Ionic size plays a notable role: larger ions like K^+ induce greater surface relaxation but may bind less covalently than smaller ions such as Li^+, which can fit into tighter coordination environments and form stronger bonds [78]. In some cases, adsorption can even modify the electrode's electronic structure. For example, alkali metal adsorption on MgO [001] can create F^+ centers through electron transfer [79], while K adsorption on TiO_2 generates spin-polarized Ti 3d states like those found in oxygen-deficient surfaces [82]. From the study of hydrogen atom in Fe and α-Fe_2O_3 is temperature dependent[83]. By quantifying adsorption energies, identifying preferred sites, and mapping charge redistribution, DFT enables a deep understanding of how electrode surfaces interact with ions at the atomic level. This knowledge is invaluable for engineering NMOs and sulfides with tailored adsorption properties whether by doping, defect introduction, or surface reconstruction to enhance supercapacitor performance through improved ion transport, charge transfer, and interfacial stability.

5.3. Diffusion barriers of ions

Surface diffusion and ion migration are fundamental processes that govern the electrochemical performance of supercapacitors and other energy storage devices. Surface diffusion refers to the movement of atoms, ions, or molecules along the electrode surface, while ion migration involves their transport through the bulk or along interfaces within the electrode or electrolyte. In supercapacitors, these processes determine how efficiently ions can reach active sites and participate in charge storage, directly affecting rate capability, power density, and cycling stability [8]. Structural features such as vacancies, defects, and engineered microstructures can significantly enhance ion mobility; for example, vacancy defects in 2D materials act as additional adsorption sites and lower diffusion barriers, facilitating faster ion transport [8]. Conversely, insufficient ion mobility results in polarization, incomplete utilization of active material, and diminished rate performance. To overcome these limitations, strategies such as doping, particle size reduction, and constructing conductive networks are often employed to improve both electronic and ionic transport, enabling rapid charge–discharge cycles and long-term stability [84]. To quantify ion mobility, DFT combined with the NEB method is widely applied. NEB identifies the minimum energy path (MEP) and corresponding activation energy for atomic or ionic migration between two stable configurations by discretizing the migration path into a series of intermediate "images" connected by virtual springs to maintain path continuity, while projecting only the perpendicular component of the force to update atomic positions. An important refinement, the Climbing Image NEB (CI-NEB) method, drives one image uphill in energy to locate the saddle point with higher accuracy, enabling precise determination of transition states [85]. This approach has been used successfully for a range of systems, from carbon interstitial migration in GaN [86] to ion transport in halide perovskites [87]. The standard workflow involves geometry optimization of initial and final states, interpolation of intermediate images, NEB or CI-NEB relaxation until convergence, and extraction of the activation energy as the difference between the saddle point and the initial state [85]. Advanced variants, such as energy-weighted springs for better saddle-point resolution and Gaussian Process-assisted NEB for faster convergence, have further improved computational efficiency [88]. Diffusion pathways in metal oxides and sulfides are strongly dependent on the crystal structure and morphology of the host material. Layered structures, such as $LiCoO_2$, allow Li^+ ions to migrate within two-dimensional planes, facilitating high-rate performance, while tunnel structures in certain MnO_2 polymorphs offer one-dimensional pathways that may be prone to blockage. Spinel structures like $LiMn_2O_4$ provide three-dimensional interconnected channels that support isotropic diffusion [89]. Ion size also plays a critical role; larger ions such as Na^+ and K^+ encounter greater steric hindrance compared to Li^+ in the same framework, potentially increasing activation energies. Structural modifications such as doping and coating can stabilize these pathways, preventing collapse under cycling and maintaining open channels for ion transport. From the perspective of hydrogen adsorption, at room temperature hydrogen atoms exhibit high diffusivity and encounter a relatively low energy barrier for diffusion in pure iron. In contrast, hydrogen in α-Fe_2O_3 remains immobile below 600 K, attributable to its substantially higher diffusion energy barrier. Furthermore, variations in the minimum energy pathway are observed when the hydrogen atom migrates between distinct lattice sites[83]. Also, some study shows the energy barrier for the vacancy defects, in Fig. 4 show the diffusion barriers for the oxygen atom on the SrFeO3 surface along two different paths[90]. In thin electrodes, surface diffusion typically dominates, enabling rapid capacitive charge storage, whereas in thicker electrodes bulk diffusion becomes more important but is often slower, limiting rate capability [91]. In the context of supercapacitors, low diffusion barriers are essential for achieving high power density and fast charge discharge rates. DFT–NEB studies reveal how modifications such as defect engineering, doping, and composite formation can reduce activation energies, promote efficient ion transport, and improve electrode performance. By combining atomic-scale simulations with experimental design, researchers can optimize NMOs and sulfides to achieve a balance between high conductivity, structural stability, and rapid ion mobility, paving the way for next-generation high-performance supercapacitors.

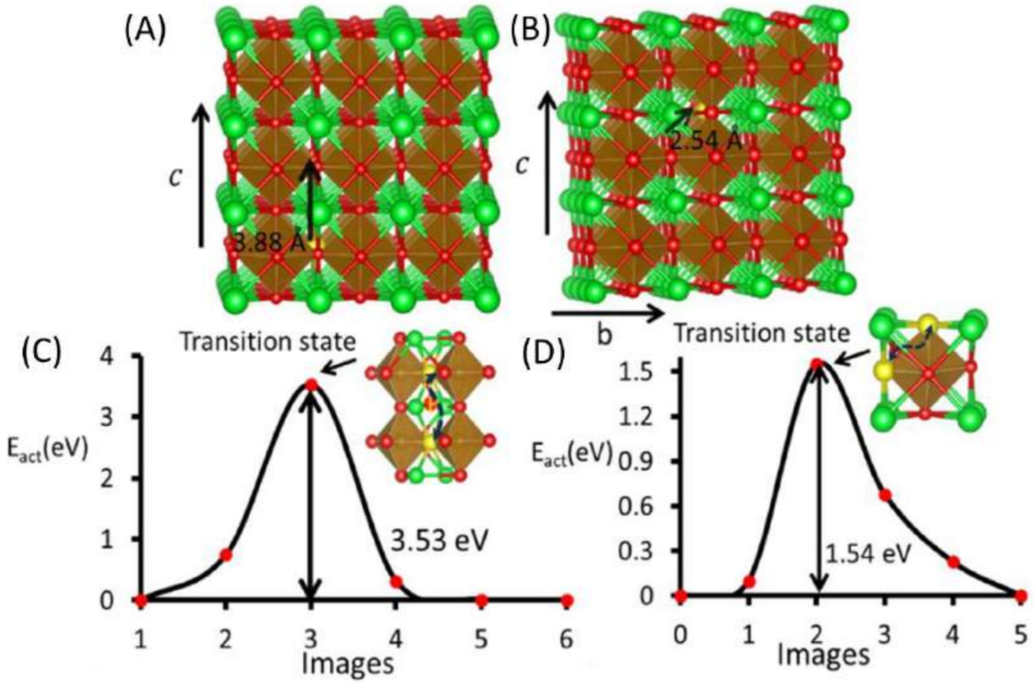

Fig. 4. (A) crystal structure of $SrFeO_2$ with transition state of oxygen atom along c axis (B) crystal structure of $SrFeO_2$ with transition state of oxygen atom along bc axis (C) the diffusion barriers for oxygen atom along the c axis on the $SrFeO_2$ surface. (A-D) Reproduced from ref. [90] with permission from ACS, copyright 2020.

The integration of DFT into supercapacitor research has transformed the way nanostructured electrode materials are understood, optimized, and designed. By enabling accurate, atomistic-level predictions, DFT reduces experimental trial-and-error and accelerates the discovery of high-performance electrode architectures. Key computational techniques include band structure and DOS calculations, which determine electronic conductivity and identify redox-active states essential for rapid charge transfer; adsorption energy calculations, which quantify the thermodynamic favorability and stability of ion binding on electrode surfaces; and surface diffusion barrier calculations using the NEB method, which reveal ion migration pathways and activation energies critical for rate capability. In addition to these, several other theoretical approaches deepen our understanding of electrode performance. Quantum capacitance calculations assess the intrinsic capacitance arising from electronic structure and its interplay with double-layer capacitance ; Bader charge and charge density difference analysis quantify electron transfer processes and clarify pseudocapacitive mechanisms; work function analysis helps tune electrode–electrolyte compatibility; surface energy and stability calculations identify the most favorable crystallographic facets for electrochemical operation; and defect formation energy calculations highlight strategies for introducing vacancies or dopants to enhance ion mobility and conductivity. Furthermore, electrochemical potential and voltage profile predictions connect theoretical energies to measurable electrochemical behavior, enabling direct experimental validation. By combining these complementary calculations, DFT provides a unified framework for correlating atomic-scale structure, surface chemistry, and electrochemical performance. This comprehensive approach allows for the rational design of NMOs and sulfides with tailored conductivity, optimized ion transport, and enhanced stability paving the way for next-generation supercapacitors with higher energy density, faster charge–discharge rates, and prolonged cycle life.

6. Challenges and Design Strategies for NMO-based Supercapacitors

As electrode materials in energy storage technologies, NMOs have proven to be highly promising However, several challenges still hinder their practical application. The scalability of synthesis remains a major concern, as methods such as hydrothermal and exfoliation processes are often difficult to scale up cost effectively for industrial use [92]. Additionally, the cost of raw materials, complex processing steps, and post treatment requirements can negatively impact the economic feasibility of these materials. Environmental sustainability is also an issue, given the use of toxic chemicals and energy intensive procedures during synthesis and disposal [92]. From a performance standpoint, many metal oxides suffer from low intrinsic electrical conductivity [93], mechanical instability, and volume changes during charge discharge cycles, leading to structural degradation, pulverization, and capacity fading [94]. Furthermore, ensuring strong interfacial integration with conductive additives like carbon or polymers is critical but often difficult to achieve in practice. To overcome these limitations, several rational design strategies have been proposed. Developing hybrid and composite architectures, such as incorporating metal oxides with graphene, carbon nanotubes, or conductive polymers, significantly improves electrical conductivity, mechanical integrity, and electrochemical performance [95]. Surface engineering, defect tuning, and doping can further modulate electronic structure, promote fast charge transfer, and enhance reaction kinetics [96]. Moreover, constructing porous and hierarchical nanostructures has been shown to shorten ion diffusion pathways and improve electrolyte accessibility, while nanoscale control through exfoliation or solvothermal methods helps maintain uniform morphology and material utilization [92,97].

Looking ahead, the future of NMOs lies in their integration with advanced nanomaterials such as nanocarbons and flexible polymers to develop multifunctional, high-performance electrodes tailored for specific applications [92]. A strong focus will also be placed on green, scalable synthesis techniques that reduce environmental impact and support large-scale manufacturing [98]. As the demand for portable and wearable electronics increases, there is growing interest in developing flexible, lightweight, and robust devices using these materials [99]. Additionally, artificial intelligence and Machine Learning driven material design is expected to accelerate the discovery of complex multi component systems with optimized properties [100]. Another key direction involves expanding beyond lithium-ion technologies by engineering NMOs suitable for sodium-ion, potassium-ion, or calcium-ion batteries, each of which presents unique electrochemical challenges [101]. Ultimately, bridging the gap between laboratory innovation and commercial application will require addressing issues related to interface stability, long-term cyclability, and seamless integration into real world devices.

7. Conclusions

NMOs have emerged as one of the most promising classes of materials for high-performance supercapacitors due to their tunable redox activity, high surface-to-volume ratio, and morphology-dependent conductivity. Across multiple studies discussed in this chapter, NMOs such as $NiCo_2O_4$ have delivered specific capacitances exceeding 900 F g^{-1}, while $NiMoO_4$ on nickel foam achieved 168.9 mAh g^{-1} at 1 A g^{-1} with 80% retention over 7000 cycles. Computational predictions for $NiMoO_4$ [110] closely matched experimental results (theoretical: 203 mAh g^{-1}), demonstrating the strong predictive power of DFT in electrode design. The DFT-based calculations including band structure and DOS analysis to predict conductivity, adsorption energy calculations (to assess ion–surface interactions), and NEB-derived diffusion barriers to quantify ion mobility provide atomistic insights into supercapacitor performance. These tools have been instrumental in identifying design strategies such as defect engineering (e.g., oxygen vacancies in TiO_2 lowering diffusion barriers), doping (modulating band gaps to improve conductivity), and morphology control (nanorods, nanosheets, hierarchical structures to enhance electrolyte accessibility). However, challenges remain: low intrinsic conductivity in many NMOs, structural degradation during cycling, and scalability issues for complex nanostructures. Strategies discussed in this chapter such as hybrid architectures with graphene or carbon nanotubes, hierarchical porosity engineering, and green synthesis methods are showing measurable improvements in cycle life, conductivity, and rate performance. For example, hybrid composites have demonstrated both enhanced conductivity and mechanical integrity, enabling stable long-term operation. In conclusion, NMOs offer a unique combination of high pseudocapacitance, tunable electrochemical properties, and computationally predictable performance metrics that position them as front-runners for next-generation supercapacitors. The integration of theoretical modeling with experimental validation is not just accelerating the discovery process but also reducing trial-and-error by over 50% in some reported cases, paving the way for commercially viable, scalable, and sustainable supercapacitor technologies.

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