

Emerging Materials for Sodium-Ion Hybrid Capacitors: A Brief Review

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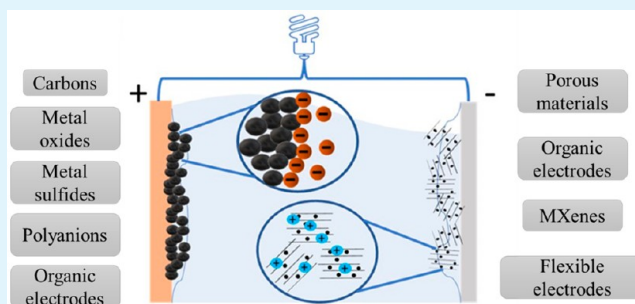
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ABSTRACT: The demand for energy storage is exponentially increasing with growth of the human population, which is highly energy intensive. Batteries, supercapacitors, and hybrid capacitors are key energy storage technologies, and lithium and sodium ions are critical influencers in redefining the performances of such devices. Batteries can store energy with high density, and capacitors can deliver a high power density. In addition, hybrid capacitors bridge the energy and power gap between a battery and supercapacitor by combining reactions from a battery-type electrode and a capacitor-type electrode. Sodium-ion hybrid capacitors (NICs) can combine the benefits of high power capacitors and high energy batteries at a cost potentially lower than that of Li analogues. However, research on NICs is in the nascent stage and requires significant attention to enable their use in practical applications. This review presents a comprehensive summary of the development of Na-ion hybrid capacitors based on carbon materials, a sodium superionic conductor NASICON, and metal oxide or sulfide-type anodes, with a particular emphasis on the performance metrics. Furthermore, design strategies and unsolved issues in emerging capacitor systems, such as pseudocapacitive electrodes, organic electrodes, MXenes, and flexible capacitors, which could be trend setters for next-generation applications, are the focus. The revolving issues with each system and the strategies to overcome such issues are also briefly discussed. A perspective and outlook on the future of NICs will help the scientific community direct their future studies.

KEYWORDS: hybrid capacitor, energy storage, emerging materials, batteries, capacitors, flexible devices, MXenes, carbon



INTRODUCTION

Modern society, with its numerous gadgets and machines for easier living, is highly energy-dependent. However, to protect the environment, the source of energy should be sustainable and from renewable sources. At present, these renewable energy sources are not evenly distributed, and their cost also differs geographically. Additionally, renewable energy sources, such as solar and wind, depend on the weather. Thus, the requirement for energy storage devices becomes eminent and inevitable. At present, electrochemical energy storage devices, such as batteries and supercapacitors, are widely used. For example, a battery stores energy from remote solar farms or windmills, and supercapacitors are used in regenerative braking to conserve energy for electric mass transportation (e.g., trams and buses).¹ The dominant storage technology, lithium-ion battery (LIBs), uses a Li-ion containing transition metal oxide cathode and graphite anode, and the Li ions shuttle between the anode and the cathode during the charge–discharge process. LIBs can store a considerable amount of energy ($>300 \text{ W kg}^{-1}$, based on cell level) but take a long time to charge due to their low power density ($<350 \text{ W kg}^{-1}$).^{2–4} In contrast, electrical double-layer capacitors (EDLCs) can

charge much faster ($>10 \text{ kW kg}^{-1}$) due to their simple nonfaradic surface reactions but have a smaller storage capacity ($5\text{--}10 \text{ Wh kg}^{-1}$).^{5,6} However, a device combining the benefits of high energy density batteries and high power EDLCs have not been realized, decreasing the performance gap between batteries and capacitors.

To bridge this gap, Amatucci et al.³ systematically constructed a lithium-ion hybrid capacitor (LICs) by combining a battery-type anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and a capacitor-type cathode (activated carbon). Typically, hybrid ion capacitors store energy through a combination of faradic intercalation/deintercalation (anode) along with simultaneous nonfaradic surface adsorption/desorption (cathode).^{5,7–9} The scheme of the working mechanism of a hybrid-ion capacitor is shown in Figure 1a. Following that, several materials (TiO_2 ,

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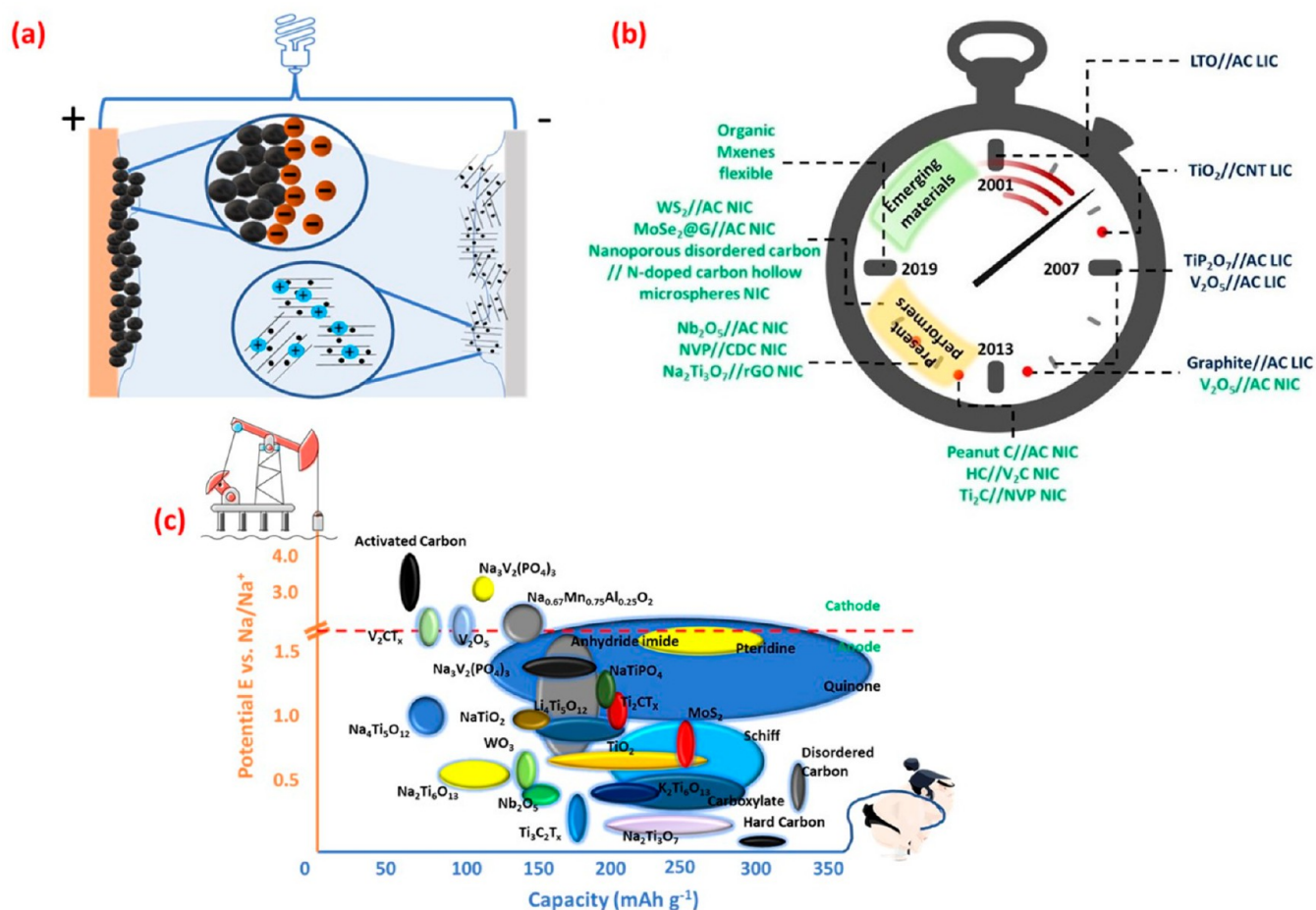


Figure 1. (a) Schematic of working mechanism of sodium-ion capacitors. (b) Timeline of various significant ion capacitors. (c) Capacity vs potential plot of commonly used electrodes in various NICs.

SnS₂, V₂O₅, Fe₂O₃, hard carbon, graphite, VN, etc.) were studied for LIC. Since then, LICs have reached an energy density close to that of a battery using high-capacity battery-type anodes and robust capacitive-type cathodes. Even hybrid-ion capacitors based on other configurations are also proposed. However, increasing demand and the cost of lithium-ion resources have greatly increased the energy cost of Li-ion-based technologies, opening the need for low-cost energy storage technologies.

Sodium-ion-based energy storage technologies, particularly sodium-ion batteries (NIBs), have gained much interest because the working chemistry is similar to that with lithium analogues.^{10–13} The abundant availability of sodium-ion resources and availability of electrode chemistry similar to that of LIBs shed light on commercialization of NIBs for large-scale applications. In this context, transferring the current knowledge from LICs to construct a sodium-ion capacitor (NIC) with a similar working mechanism could increase the value of hybrid-ion devices. To date, the research on NIBs are at an advanced stage, and electrodes performing equivalent to LIBs were recently demonstrated. The timeline of developing history of several important NICs is shown in Figure 1b. The research interest in NIC started when Lu and co-workers first demonstrated a 2.8 V sodium-ion capacitor with a V₂O₅ anode that showed an energy density comparable to that of Li-ion analogues.¹⁴ It was during the same period that NICs were studied with Na₂Ti₃O₇ and hard carbon anodes, opening

further studies into NICs. Mitlin and co-workers studied an ultra-high energy density NIC utilizing a hard carbon anode and an activated carbon cathode, both derived from peanut shells. The energy density of the presodiated NIC showed the highest energy–power behavior (beyond 200 Wh kg⁻¹) to date.¹⁵ In 2016, we showed that utilizing the intercalation-type anode, Na₃V₂(PO₄)₃, in NIC can greatly enhance the energy density and cyclability of NICs compared to lithium counterparts.¹⁶ During past several years, NICs have undergone a remarkable development, and NICs performing better than LICs were realized as a new class of materials that includes organic electrodes, MXenes, and flexible/free-standing electrodes.

Currently, carbon electrodes,^{17,18} intercalation/alloy-type anodes,^{16,19} NASICONs, metal selenides/oxides,^{20,21} and organic electrodes^{22–25} were widely used for NICs. The discharge capacity and working voltage of several anodes and cathodes for NIC is shown in Figure 1c. However, key scientific issues in NICs such as low anode kinetics, low cathode capacity, and a kinetic mismatch between the anode and the cathode originating from electrode materials must be clearly understood. Furthermore, the use of next-generation high-capacity anode materials and high-capacity–high-rate capacitive cathodes could push the NICs toward a high energy density with high power. The prospects and challenges of new emerging materials such as 2D/3D nanostructured carbon, high-capacity pseudocapacitive materials, MXenes, organic

electrodes, and flexible electrodes that outperform conventional electrode materials should be understood. In this review, we summarize the advances in anode and cathode materials for NICs systematically and discuss several strategies and prospects toward practical development of NICs.

■ ANODE MATERIALS

Carbon-Based Materials. Carbon is one of the most abundant and versatile elements and is well-known for its flexibility. This versatility appropriately fits the battery requirements; thus, many high energy anode materials for hybrid capacitors are based on carbon (Figure 2). Graphite,

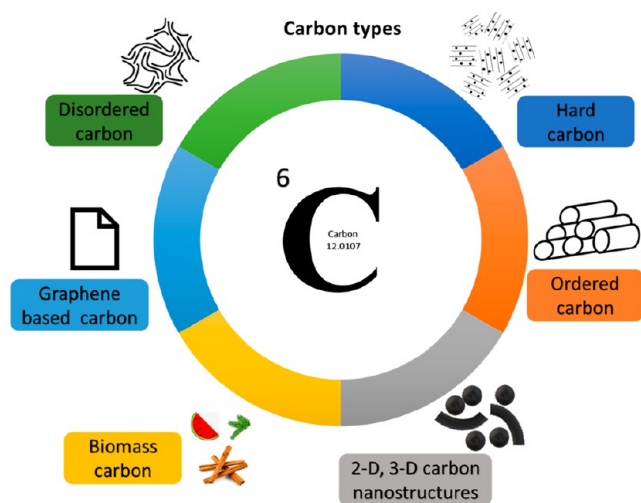


Figure 2. Different carbon types used as high-performance carbon electrode materials.

the most successful anode material in LIBs and LICs does not support the intercalation reaction with Na^+ ions. However, Kang and co-workers revealed a reversible Na^+ -ion insertion into graphite through solvated Na^+ -ion co-intercalation reactions.^{26,27} They further revealed that the voltage of sodium-ion storage in graphite is dominated substantially by ternary graphite intercalation compounds and free solvent activity. Wang and co-workers also revealed the Na^+ -ion insertion into expanded graphite, which is a long-range-ordered layered structure analogous to graphite.²⁸ Expanded graphite with a large interlayer lattice distance (4.3 Å) can reversibly store Na^+ ions and deliver a high reversible capacity of 284 mAh g⁻¹. These studies have shed light on the utilization of graphite-based anodes for NICs. Graphite anodes have exhibited an energy density of 60.5 Wh kg⁻¹ and a maximum power density of 17,127 W kg⁻¹ when employed in NICs.²⁹ Similarly, electrochemically exfoliated graphite, boron-doped graphite sheets, and expanded graphite have also been studied for NICs and have delivered an energy density of approximately 90 and 104 Wh kg⁻¹, respectively.^{30,31} However, the cycle of NICs based on graphite anodes are reported to be lower than 5000 cycles. The low cycle life of graphite anodes can be attributed to irreversible reactions between the surface and electrolyte to form a solid electrolyte interface (SEI). A nonuniform SEI layer formation can induce more irreversible reactions in consecutive cycles, reducing the efficiency of the anode.

Various carbon materials based on hard carbon, graphene, carbon sheets, carbon quantum dots, and nanostructured

carbon were successfully studied as an anode for NIBs and NICs. The prominent Na^+ storage mechanism in a carbon anode was based on the combination of the Faradaic and non-Faradaic processes. The Na^+ -ion insertion into expanded graphitic structures of carbon is generally diffusion-limited, and adsorption occurs on the surface defects/functional groups and voids. Yao et al.³² were the first to report a hard-carbon-based hybrid capacitor, which comprises a presodiated hard carbon and activated carbon as the anode and an EDLC-type cathode, respectively. Presodiation is essential in carbon-based NICs to overcome the initial sodium-ion loss due to SEI layer formation and electrolyte decomposition. In addition, they demonstrated both Li and Na ions HC parallel at a subtle current density of 2 mA cm⁻² for 1000 cycles. In comparison, it can be observed that Li ions outperform Na ions by 97 and 91% in terms of capacity retention, respectively. This was an indirect demonstration of the problems with Na ions at that time. Moving forward to 2015, the NHC started to gain momentum, beginning with a report by Wang et al.,²¹ whose high energy sodium capacitor based on peanut-shell-derived carbon for both the anode and cathode drew the attention of many researchers toward NIC. They were able to achieve an extremely high energy density of 201 Wh kg⁻¹ and demonstrated a stability for more than 10,000 cycles. This energy density remains a benchmark that many groups are attempting to reach. As a major advantage of this study, the authors used peanut-shell-derived carbon, which is a naturally occurring biowaste, and successfully demonstrated a hybrid capacitor. The energy density reported was on par with a lithium-ion counterpart that has attracted the attention of many research groups exploring NICs. Another NIC with an energy density of 168 Wh kg⁻¹ was reported by Wang et al.³³ Instead of an intercalation-type electrode, the authors used nanoporous carbon and microporous graphene as negative and positive electrodes, respectively. Although liquid electrolytes have commonly been used, they demonstrated the advantage of a gel polymer electrolyte over liquid. Although gel polymers have been less explored for Na batteries, they have been extended to the same hybrid capacitor and demonstrated a high energy output. Using a gel electrolyte, a cell voltage of approximately 4.2 V was achieved, enabling a high energy density. The main disadvantages that emerged were the use of a microwave-assisted synthesis, which cannot be scaled up beyond a certain limit, and the use of KOH for activation. Later, Mitlin et al.³⁴ fabricated a hybrid capacitor using peanut-skin-derived carbon nanosheets with nanometer thickness following the same source, i.e., peanut shells, but from a different product. Unlike a previous report, peanut skin can only deliver a maximum of 112 Wh kg⁻¹. Peanut skins are distinct from peanut shells, which are lignin-rich materials, and can form ordered carbon extremely easily. In comparison to previous studies, the energy density reported is only 66% in terms of both energy density and cycle stability. This report indicates that the success of earlier studies have drawn the attention of various groups toward NIC. In the same year, Ding et al.³⁵ also reported a hybrid capacitor using N- and O-functionalized carbon, which displayed a similar energy density of 111 Wh kg⁻¹, with a capacity retention of up to 90% for 5000 cycles. In comparison to previous years, the energy density achieved was 66%, but other possibilities for the synthesis and functionalization of carbon materials were explored. With new groups exploring NICs, the energy density was significantly improved by 30–50 Wh kg⁻¹ using various

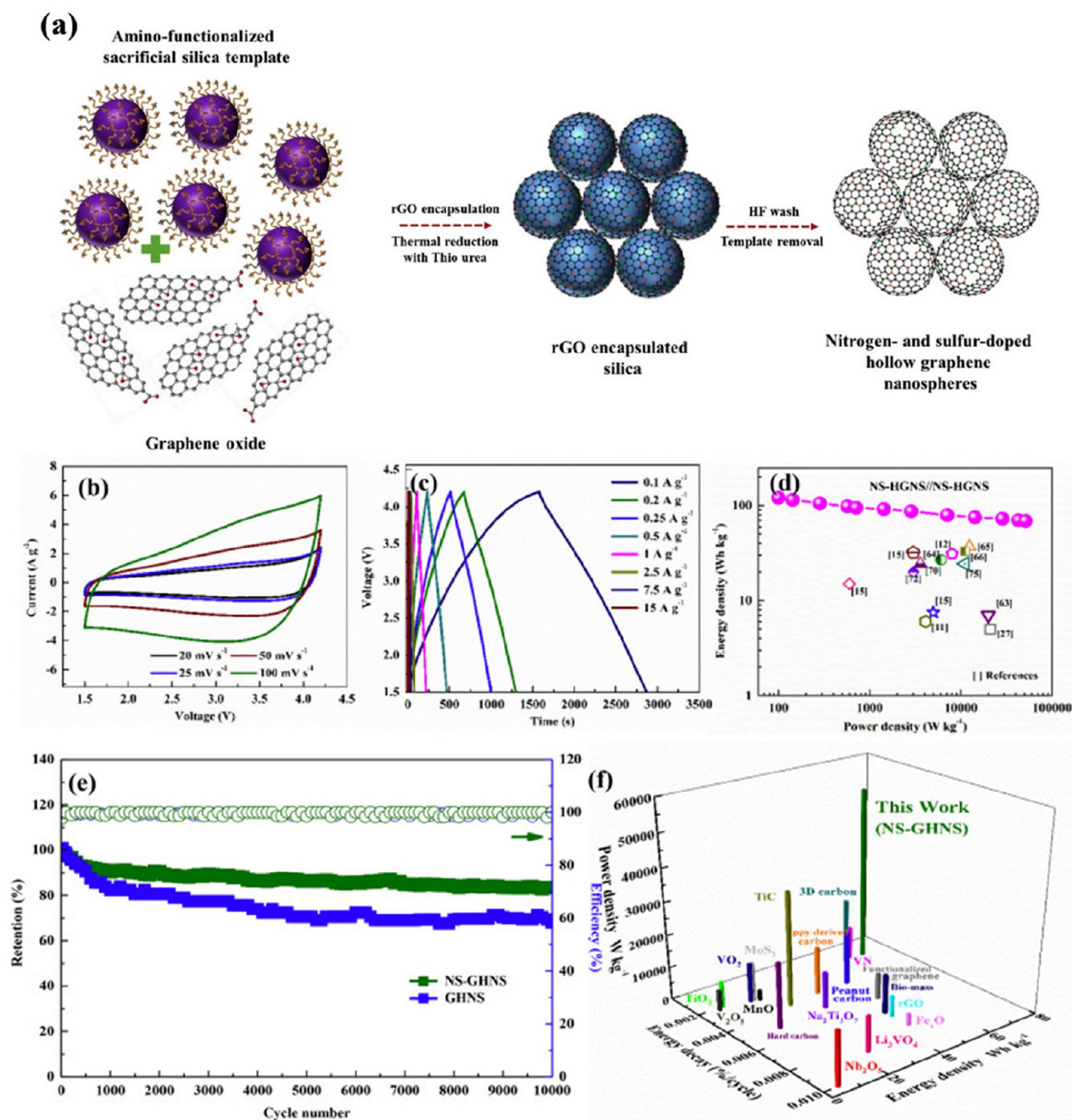


Figure 3. Schematic of hybrid ion capacitor constructed by Thangavel et al.¹⁸ (a) Preparation of heteroatom-functionalized 3D graphene spheres. (b–e) Electrochemical performance of constructed NICs, including cycle stability, and (f) performance comparison with earlier reports. Reprinted with permission from ref 18. Copyright 2020 Elsevier.

new materials and techniques. In a report by Song et al.,³⁶ the effect of pseudographitic layers in the carbon structure was exploited by coupling hierarchically porous carbon nanoweb with functionalized carbon nanosheets. This nanoweb carbon can achieve an energy density of 130.6 Wh kg^{-1} , with capacity retention for a few thousand cycles. Although highly porous carbon nanoweb were obtained, the synthesis procedure was tricky with freeze-drying, probe sonication, and KOH activation, which makes it a difficult candidate for a scale-up. In the same year, another report by Wang et al.³⁷ described the

synthesis of N-doped carbon hollow microspheres using the sol–gel coating process, thereby achieving a high degree of uniformity and porosity. Additionally, this was among the few early studies that used density functional theory (DFT) to analyze the effect of doping in the interaction sites of Na ions, providing insight into the working mechanism of battery-type electrodes. Thus, the constructed hybrid capacitor can achieve an energy density of 157 Wh kg^{-1} with a cycle stability of over 1000 cycles. In addition, the working voltage was pushed to 4.4 V with a gel polymer electrolyte. Thus, in comparison with the

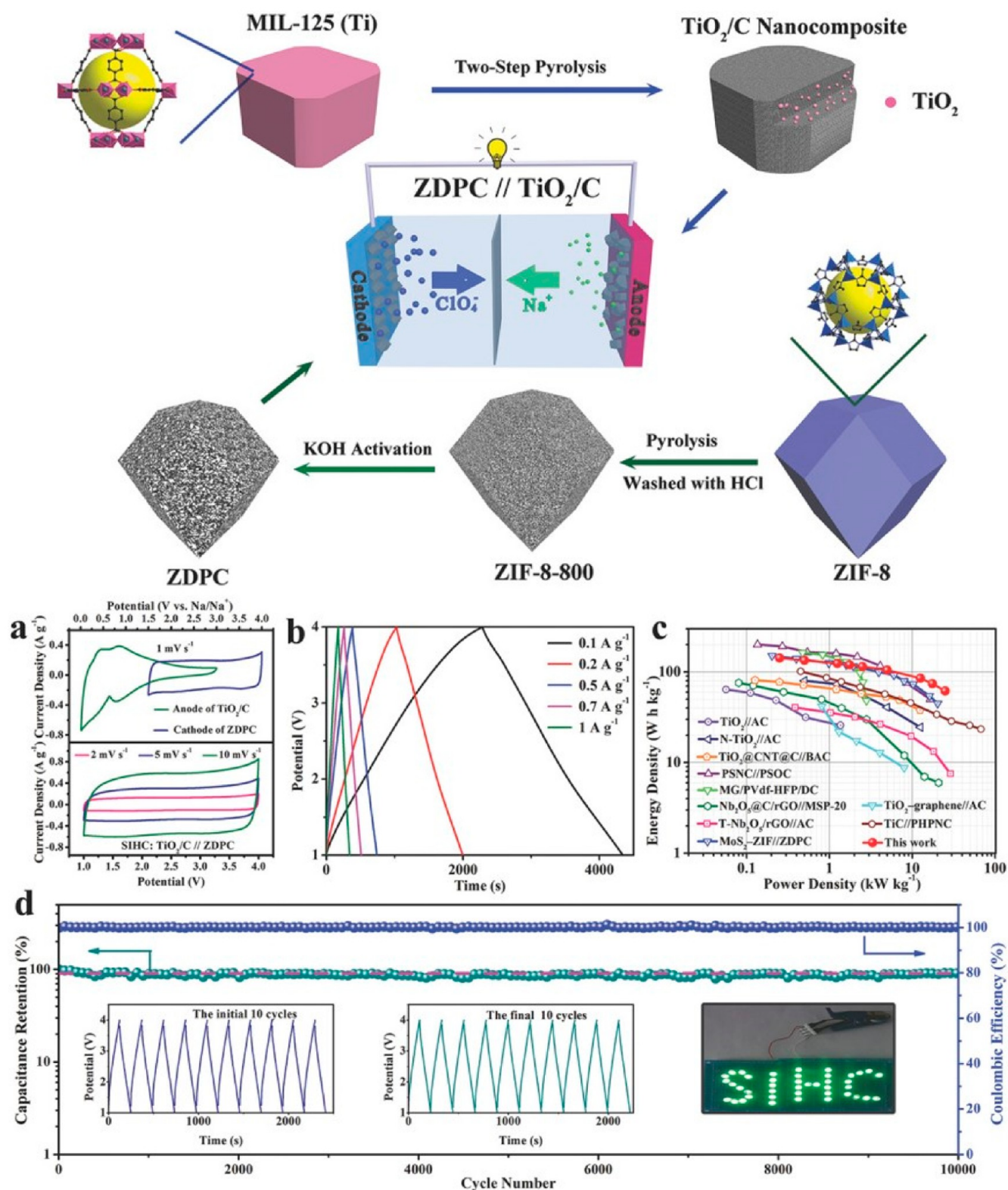


Figure 4. Top: Schematic of hybrid ion capacitor constructed by Yan et al., including the process of MOF synthesis. Bottom: Electrochemical performance of Na-ion capacitor employing a TiO_2 anode and MOF-derived carbon cathode (ZDPC): (a) cyclic voltammetry (CV) curves of TiO_2 and ZDPC in a sodium half-cell (top) and CV curves of NIC at various scan rate (bottom). (b) Galvanostatic charge-discharge profiles of NIC. (c) Ragone plots of NIC compared with several other systems. (d) Cycle life of NIC. Inset curves: charge-discharge profiles of NIC, and the digital photograph showing the lit LED arrays by the NIC device. Reprinted with permission from ref 56. Copyright 2018 Wiley.

previous year, the energy density was improved to 150 Wh kg^{-1} , and significant improvement was made to the voltage

window using a gel polymer electrolyte. Although a few other studies were unable to achieve a high energy density

comparable to that from the previous year, they are worth mentioning due to their efforts to synthesize various carbon materials, such as the metal-organic framework (MOF)-based NIC developed by Zhang et al.,³⁸ carbon from recycled olive pits developed by Ajuria et al.,³⁹ and tremella-like N,O-codoped porous carbon developed by Niu et al.⁴⁰ In the next year, Ding et al.⁴¹ reported nanotube-like hard carbon synthesized through high-temperature carbonization of polyaniline (PANI) for NICs. The NIC demonstrated a high energy density of 133 Wh kg⁻¹ and stability for more than 12,000 cycles. The main advantage was an easier synthesis of a nanotube-like carbon material by simple carbonization and activation. The synthesis technique did not involve a complex process, such as templating. A similar energy density of 133 Wh kg⁻¹ with a high power output was demonstrated by Wang et al.⁴² using a 3D carbon framework anode synthesized through the electrolysis of ethanol/NaOH with Pt and Ti electrodes. Although the procedure is simple and innovative, the electrolysis process is energy intensive, and Pt is used as an electrode. Graphene is a carbon analogue used in a wide variety of applications and is well-known for its high structural stability and conductivity, which can be modified based on the requirements. Using graphene, Li et al.⁴³ synthesized carbon spheres and 2D functional carbon through a simple heat treatment of a biomass (glucose). The NIC constructed using these carbons can deliver a high energy density of 182 Wh kg⁻¹, which is 33% higher than the benchmark of the previous year. Although this NIC can deliver an extremely high energy density, a stability of at least 10,000 cycles is yet to be reported. This yearly benchmark was further increased to 245 Wh kg⁻¹ by Chen et al.,⁴⁴ who achieved such an ultrahigh energy density using N-doped porous hard carbon and a dual ion strategy. This new and innovative dual ion (Na⁺ and N, where N acts as the functional group) strategy achieves an extra energy density, with faster charging time and slower discharge time, making it relatively suitable for practical applications. Although this system can deliver an extremely high energy density, a stability of only 1000 cycles was demonstrated. In later years, a similar trend of high energy density with less cycle stability was observed in other reports.^{45–47}

By contrast, a few notable studies have achieved an extremely high power density suitable for faster energy storage; for example, Shen et al.⁴⁸ used an N-doped graphdiyne material, which delivered a remarkable power density of 22,500 W kg⁻¹ in an NIC configuration. This was further advanced by Thangavel et al.,¹⁸ who utilized heteroatom (nitrogen and sulfur)-enriched graphene hollow spheres as both anode and cathode. The kinetic mismatch between the kinetically poor intercalation anode and the kinetically superior capacitor-type electrode was overcome by designing the bifunctional electrodes. The nitrogen and sulfur atoms in the 3D carbonaceous matrix boosted the Na-ion storage capacity and anion storage ability of the electrodes. This faster ion transport delivered an even higher power density of 51,000 W kg⁻¹, which can be quite suitable for low energy density, fast-charging applications, such as wearable technologies and mobile batteries (Figure 3). Further engineering the functional groups, size, and morphology of 3D nanocarbons can bridge the performance gap between batteries and capacitors. Thus, there are a few noteworthy reports that demonstrate a high power density of more than 20,000 W kg⁻¹ but with lower energy density.^{40,47,49,50}

Metal Oxides. Metal oxide anodes for a sodium-based hybrid capacitor have their roots in sodium-ion batteries (NIBs). NIBs prominently apply metal oxides because they have capacity higher than that of carbon analogues. In 2012, Augustyn et al.⁵¹ demonstrated the first metal oxide based NIC using V₂O₅/CNT for a high-capacity vanadium oxide, the conductivity of which was enhanced by the CNT architecture. The cell was operated between 0 and 2.8 V in an organic solvent electrolyte. Compared to an earlier reports, the energy density was better than that of many EDLC capacitors at the time. Using a metal oxide/carbon architecture, the cell delivered an energy density of 38 Wh kg⁻¹ and exhibited more than 75% capacity retention after 1000 cycles. Over the next 4 years, only a few significant improvements were made in NIC, apart from the study by Zhu et al.,⁵² who used Nb₂O₅ and peanut shells as the anode and cathode, respectively. The NIC can deliver an energy density of 43 Wh kg⁻¹ and a better stability of more than 3000 cycles. Since 2017, NIC-based Ti compounds have started gaining attention, and many reports with high energy and power densities are being reported. Ti-based compounds have been the most studied anode for NICs after carbon-based anodes owing to their excellent safety, natural abundance, and low cost. Unlike high-voltage Li⁺ intercalation with TiO₂, Na⁺ ions undergo intercalation at a lower potential, making it favorable for achieving a high energy NIC. However, the poor electron mobility ($\sim 10^{-12}$ S cm⁻¹), SEI layer formation at low voltage, and low sodium-ion diffusivity of the TiO₂ anode limits its rate capability. Thus, various strategies, such as nanostructuring, nanocarbon composite/coating, and aliovalent doping, have been adopted by various groups to overcome this deficiency. These engineered TiO₂ anodes can perform extremely well with discharge capacities of >300 and >50 mAh g⁻¹ at a low and high current (30 A g⁻¹), respectively, as well as an excellent stability (>1000 cycles). However, non-engineered TiO₂ delivers a low discharge capacity (<150 mAh g⁻¹) even at low current rates, including poor cycle life (50 cycles). In 2016, Liu et al. reported a N-doped TiO₂ nanosphere as an anode material for ion capacitors.⁵³ Thus, a constructed ion capacitor with activated carbon (AC) as the cathode can deliver a higher energy density and high power density of 80.3 Wh kg⁻¹ and 12,500 W kg⁻¹, respectively. A high energy density was able to be harnessed by N-doping and a nanosphere shape morphology, which addresses the key issues of low conductivity and low ion diffusivity, respectively. To address these issues, other groups have attempted similar approaches, such as nanoscale morphology and improving the conductivity by doping. By making a carbon nanotube (CNT) nanorod composite, Zhu et al.⁵⁴ achieved power density of 81.2 Wh kg⁻¹, which was further improved to 94.7 Wh kg⁻¹ using a TiO₂/R-GO composite by Wang et al.⁵⁵ This was further increased to 142.7 Wh kg⁻¹ by Li et al. by applying a MOF-based Ti anode.⁵⁶ Notably, this morphology improves the energy density and exhibits an extremely high power density of 25 kW kg⁻¹, with a significant lifespan of more than 10,000 cycles (Figure 4). Although the material displayed a superior performance, a drawback lies in the large-scale MOF synthesis and the expensive precursors used. This was further enhanced to 158 Wh kg⁻¹ using S-doped TiO₂ nanosheets by Kang et al.⁵⁷ and was demonstrated at a low temperature of -20 °C, which was the first of its kind.

Sodium-ion containing layered oxide-type anodes were also extensively studied as intercalation-type anodes for NICs.

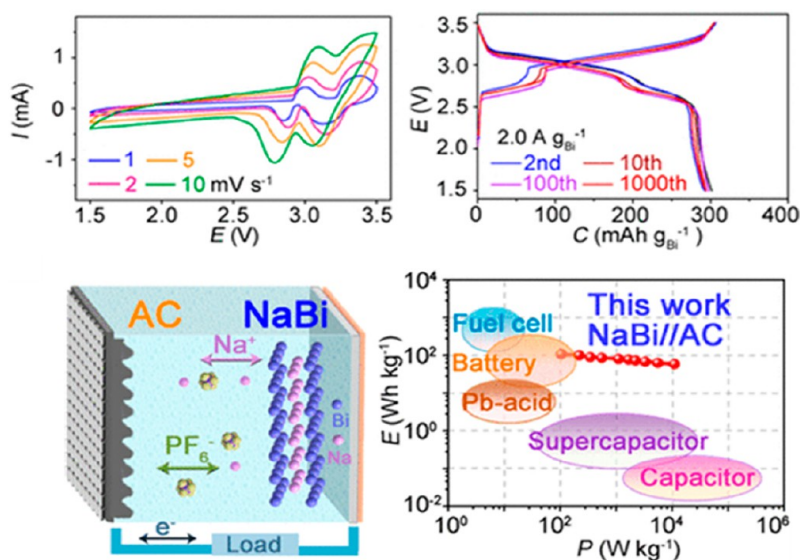


Figure 5. Anodic performance of nanoporous NaBi anode for sodium-ion batteries and performance of NIC constructed by coupling NaBi anode and activated carbon cathode. Reproduced from ref 72. Copyright 2018 American Chemical Society.

$\text{Na}_2\text{Ti}_3\text{O}_7$ can accommodate $\sim 3.5 \text{ Na}^+$ to deliver a theoretical capacity of $\sim 310 \text{ mAh g}^{-1}$, which is slightly higher than that of TiO_2 . The strong covalent bonding in TiO_6 octahedra and two-phase Na^+ -ion storage in $\text{Na}_2\text{Ti}_3\text{O}_7$ with a $\sim 0.3 \text{ V}$ working voltage can output a high energy density NIC and a long cycle life. Wang et al. first proposed a $\text{Na}_2\text{Ti}_3\text{O}_7$ -based insertion-type electrode as an anode for NIC.^{58,59} To enhance the rate performance, the $\text{Na}_2\text{Ti}_3\text{O}_7$ was synthesized into nanotubes for a large surface area with open tunnel structures and a short diffusion path for intercalation and deintercalation. Thus, a hybrid capacitor with activated carbon was constructed that could deliver 34 Wh kg^{-1} with a power density of 889 W kg^{-1} . In addition, this was one of the early studies to propose the sodium-ion capacitor concept. In 2015, the same materials were further upgraded into $\text{Na}_2\text{Ti}_3\text{O}_7@\text{CNT}$ coaxial nanocables⁶⁰ by Zhang et al., who delivered a high rate capability and cycle stability. The improved performance benefitted from a unique 1D nanostructure and the presence of a pseudo-charge-storage mechanism. Thus, the constructed hybrid capacitor can improve the energy density to up to 58.5 Wh kg^{-1} and provide a high power density of 3000 W kg^{-1} . Metal oxides based on another transition metal chemistry were also studied for NIC applications.

Vanadium oxide xerogels with a large interlayer distance can deliver extremely high capacity of up to 338 mAh g^{-1} but are limited by their poor stability. Thus, by coupling them, NIC can deliver an energy density of 194 Wh kg^{-1} ; however, the stability was inferior, which can be attributed to the cathode material.⁶¹ NIC based on a $\text{MoO}_2@\text{rGO}$ composite anode delivered energy and power densities of 79 Wh kg^{-1} and 95 W kg^{-1} , respectively.⁶² Bimetallic oxides were also studied as an anode for NIC application. A 3 V NIC constructed with spinel NiCo_2O_4 as an anode and an activated carbon cathode delivered energy and power densities of 13.8 Wh kg^{-1} and 308 W kg^{-1} , respectively, including 61.2% energy retention after 2000 cycles.⁶³ In another report by Minakshi et al.,⁶⁴ magnesium molybdate (MgMoO_4) was used as the anode material with both hierarchical and porous structures. The metal oxide was derived from LIB applications where binary metal oxides are used as electrodes with high capacity.

Although Ni and Mn were other cation choices for use in molybdate, they were eventually discarded because of their poor cycle stability. Thus, the constructed NIC delivered an energy density of 250 Wh kg^{-1} ; however, similar to its alloying-type counterparts, it was again limited by a poor cyclic stability. In the following years, the energy density was limited to 185 Wh kg^{-1} at the maximum, and much of the focus was on modifying the existing materials to improve the stability by various groups.

Sulfides and Alloy-Based Anodes. Despite their high theoretical capacity, metal oxides exhibited inferior reversible capacity and poor sodium-ion kinetics. Anodes based on metals, metal sulfides, and selenides have gained considerable attention owing to their high discharge capacity from multielectron reactions involving insertion, conversion, and alloying reactions.^{65,66} The weaker metal–sulfide bond in sulfide-based anodes (weaker than the homologous metal–oxygen bond in metal oxides owing to the different electronegativity of S and O) can facilitate chemical reactions during the charge–discharge cycle. The discharge capacities of metals and metal sulfides are considerably higher than those of metal oxides, which is favorable for achieving high energy density NICs.⁶⁷ However, metals and metal sulfide anodes suffer from a large volume expansion during the Na^+ storage, sluggish Na^+ diffusion kinetics, and poor electrical conductivity, leading to severe capacity fading, poor cycle life, and unacceptable rate performance compared to that of metal oxides.⁶⁸ Thus, the morphologies and structures of these high-capacity anodes must be engineered to realize a highly efficient NIC.

The MoS_2 –carbon monolayer developed by Wang et al.⁶⁹ and Sb_2X_3 ($\text{X} = \text{O}, \text{S}$) developed by Cai et al.⁷⁰ delivered nearly similar energy densities of 120, 111, and 124 Wh kg^{-1} . Since 2018, significant improvements have been made in the anode capacity and overall energy density by various groups. A benchmark range of 120 Wh kg^{-1} set in the previous year was drastically increased. In a report by Gómez-Cámer et al.,⁷¹ the TiSb_2 alloy was used as an anode material because of the ability of alloying materials to store large amounts of Na ions. This was one of the earliest reported alloying-type anode materials

for use in LIBs and NIBs. This TiSb_2 alloy-based NIC could deliver an improved energy density of 132 Wh kg^{-1} but was limited by its poor 63% retention after 1000 cycles, which has been associated with alloying-type materials. Similar types of alloying materials, such as NaBi developed by Wang et al.,⁷² delivered a relatively low energy density of 106 Wh kg^{-1} but better cycle stability with 98.6% capacity retention after 1000 cycles. This superior stability was ascribed to a 3D porous network ensuring the fast kinetics during the alloying and dealloying processes (Figure 5). MoS_2 is another alloying electrode well-known for its superior capacity. In the same year, three different reports on MoS_2 displayed three different energy densities by simply modifying the morphology. Wang et al.⁷³ synthesized an ultrathin MoS_2 using solid-phase synthesis and developed a composite with a bagasse-derived carbon framework to deliver an energy density of 112 Wh kg^{-1} with a cycle stability of 5000 cycles. Unlike previous alloy type anodes, in which the stability was inadequate, this material displayed a better performance. Concurrently, Liu et al.⁷⁴ synthesized another modification in MoS_2 by making a nanocomposite with a reduced graphene oxide (rGO). Here, unlike in a previous report, the interlayer of the synthesized MoS_2 was expanded to accommodate bigger Na^+ ions and a higher ion diffusion rate. In addition, the kinetics were compared with those of Li^+ ions, and NIC was found to outperform lithium (LIC). This interlayer-expanded architecture could achieve a high energy density of 140 Wh kg^{-1} with a superior stability for 10,000 cycles. This energy density was further increased to 244 Wh kg^{-1} by Duan et al.²⁰ using a similar wide interlayer along with carbon spheres and N-doped carbon nanosheets. A Si-based templating procedure was used to form a carbon hollow sphere, which improved the ion diffusion and electrical conductivity to achieve this extremely high energy density. Although UV light irradiation was also used to improve the capacity, the drawback lies in the complicated synthesis procedure with the additional requirement of a UV light source to gain additional energy. However, metal oxide was also equally pushed for higher benchmarks by synthesizing different nanostructures and/or incorporating them in carbon architectures. For example, in metal chalcogenides, FeS quantum dots embedded in 3D carbon were used as an anode material for NIC. Metal sulfides are commonly used as anodes because of their high theoretical capacity in NIBs. However, they are limited by unstable M–S ionic bonds compared to M–O bonds; this poor stability was improved by embedding in a support structure, such as 3D carbon. The strategy was effective in terms of maintaining a high energy density of 151 Wh kg^{-1} for a 91% capacity retention until 5000 cycles. Similarly, retaining a better energy density, the cycle stability was enhanced in bimetallic sulfides by Liu et al. Using $\text{MoS}_2/\text{CoS}_2$ -RGO⁷⁵ as an anode, they achieved an energy density of 152 Wh kg^{-1} in NIC, which was improved in $\text{Mo}_2\text{S}_3/\text{NiS}_2$ -RGO to up to 182 Wh kg^{-1} , and the cycle stability was eventually improved with an 85% retention after 1000 cycles.

By contrast, metal sulfides, such as VS_2 developed by Xu et al.⁷⁶ and MoS_2 developed by Wang et al.,⁶ delivered an extremely high power density of $40,000 \text{ W kg}^{-1}$. The power density of MoS_2 was drastically improved to $103,000 \text{ W kg}^{-1}$ using interlayer-expanded MoS_2 . To summarize, in the case of metal-based anodes, an energy density higher than that of carbon analogues can be achieved; however, a high power density suitable for a fast charging requirement can be achieved

using a composite with carbon structures with little or more compromise to the energy density. In addition, the cycle stability is the most severe issue that must be addressed. Although interesting architectures, such as quantum dots and MOFs, are used for improving the stability, such techniques remain unfeasible for commercial bulk purposes. Therefore, a new approach is required to improve the cycle stability, such as the use of a gel electrolyte and mixed ion electrolyte strategy, of NIBs.

Polyanions. Similar to other types, a sodium superionic conductor, i.e., a NASICON-type electrode material used in NIBs, was also used in NICs. NASICON electrodes are of substantial interest because of their (i) high Na^+ diffusion coefficient, which facilitates a faster migration of Na^+ ions than a Li analogue, and (ii) higher structural and thermal stability compared to that of other electrode materials. NASICON consists of a $(\text{M}_2(\text{PO}_4)_3)_3$ ($\text{M} = \text{V}, \text{Ti}, \text{Fe}, \text{Mn}$) framework formed using a corner-linked $[\text{MO}_6]$ octahedral that can facilitate a rapid and facile movement of Na^+ ions. NASICON electrodes show an electrochemical activity in both anodic and cathodic regions based on the transition metal chemistry. The notable NASICON electrodes studied for NIC include $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{NaTi}_2(\text{PO}_4)_3$.

Previously, Jian et al.⁷⁷ reported the first such NIC by coupling a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) electrode as both a cathode and an anode. The key advantage of less electrolyte consumption during the charge-storage process helped to improve the energy density. The constructed symmetric NIC could deliver an energy density of 26 Wh kg^{-1} with a decent power density of 5400 W kg^{-1} . The poor and sluggish intercalation kinetics in the symmetrical capacitor system outputs an energy density inadequate compared to that of lithium analogues. To tap more energy density out of NVP, Ranjith et al.⁷⁸ coupled NVP with an eco-friendly carbon source from cinnamon sticks and constructed a hybrid capacitor system that can deliver a high energy density of 118 Wh kg^{-1} . Unlike previous reports, the NASICON electrode showed an improved ionic diffusion and kinetics owing to the presence of a uniform and ultrathin conductive carbon layer. This improved the energy density and demonstrated an extremely high stability for 10,000 cycles. Unlike in other reports, more emphasis was provided to cell balancing, which delivered superior stability and a high energy density. This energy density was further increased by Guo et al.²⁴ by supporting NVP on a carbon cloth as an anode and $\text{NaTi}_2(\text{PO}_4)_3$ (NTP), which is another NASICON-type electrode, as a cathode. The advantages here are the commercial availability of NVP and NTP as electrodes and the ability to embed them in a free-standing carbon cloth structure for possible flexible electronics applications. This hybrid capacitor can deliver an extremely high energy density of 396 Wh kg^{-1} with an extremely high power density of $97,000 \text{ W kg}^{-1}$. The proper combination of high-capacity electrode materials with a suitable conductive carbon support combined to give such a high energy, high power density hybrid capacitor. Much like metal analogues, the cycle stability was also limited to 2000 cycles. Meanwhile, another type of NASICON electrode NTP was also researched by various groups. NTP grown on graphene nanosheets was first reported by Thangavel et al.,²² who used NTP grown on a graphene nanosheet as an anode. NTP is another NASICON electrode known for its high ionic conductivity and ultrafast sodium insertion kinetics with structural stability. Much like previous

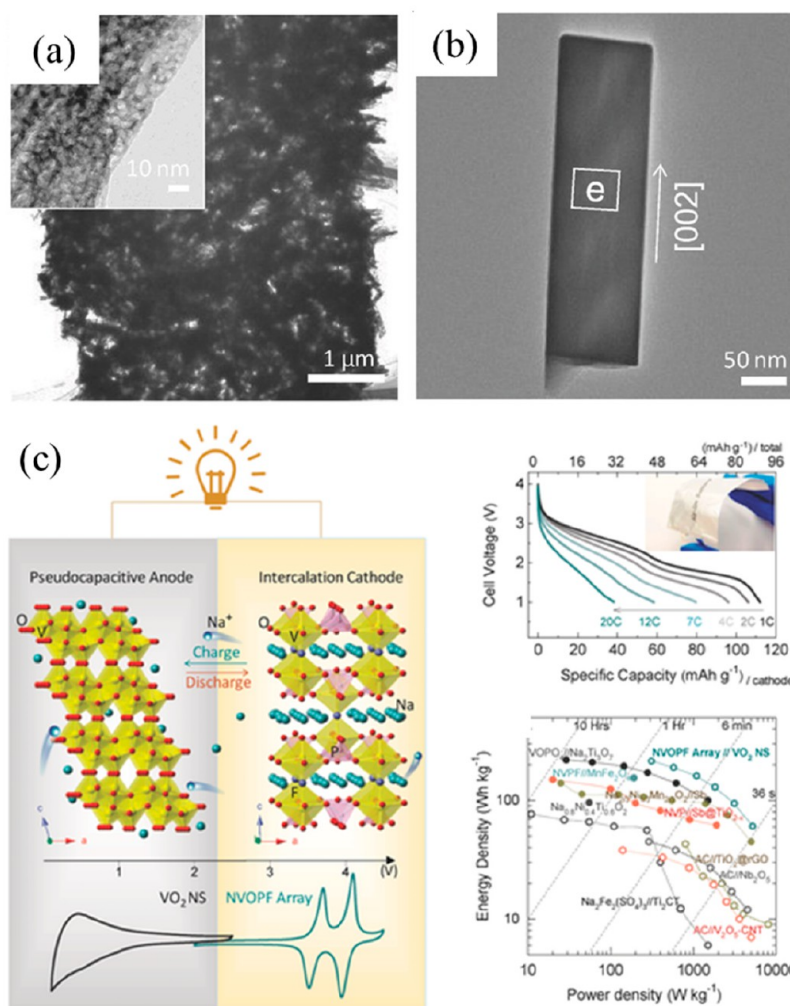


Figure 6. (a) Transmission electron microscopy (TEM) images of VO_2 nanosheets. (b) TEM image of the NVOPF nanorod. (c) Performance of sodium-ion hybrid device made with 3D flexible NVOPF array/ VO_2 nanosheets. Reprinted with permission from ref 23. Copyright 2018 Wiley.

reports combining a high-capacity NTP with a graphene-based carbon backbone, an energy density of 80 Wh kg^{-1} could be delivered with a power density of 8000 W kg^{-1} and an extremely high stability with a 0.13% capacity fade per 1000 cycles. Similar energy density ranges of 56, 53, and 56 Wh kg^{-1} were achieved using NTP nanocages,⁷⁹ an NTP microsphere,²⁵ and NTP hierarchical nanofibers,⁸⁰ respectively. Another NASICON material $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ (NVOPF) was commonly used in NIB for a high redox activity owing to the presence of F. This enhanced both the capacity and the stability of NVP and is commonly considered a second-generation material. This NVOPF was extended to a hybrid capacitor by Chao et al.,²³ who coupled NVOPF with a metal oxide nanosheet. Unlike carbon analogues or a similar NVP material used as a cathode, the metal oxide sheet was used as a cathode material for a superior energy and power density. Thus, the constructed hybrid capacitor could deliver an energy density of 215 Wh kg^{-1} with a power density of up to 5200 W kg^{-1} and a sustained stability for more than 10,000 cycles owing to the highly stable electrode materials (Figure 6). A similar high energy density of 158 Wh kg^{-1} was reported by Wu et al.⁸¹ using NVOPF@PEDOT core-shell nanorods, and a density of 182 Wh kg^{-1} was reported by Qiu et al.⁸² using NVOPF encapsulation.

To summarize, although NASICON-type materials can deliver extremely high energy densities among their counterparts, not many studies have reported a hybrid capacitor with a very high power density. Among them, Xu et al.¹⁷ used N-doped carbon nanosheets encapsulated with NVP and achieved a maximum power density of $48,000 \text{ W kg}^{-1}$ with a maximum energy density of 161 Wh kg^{-1} . Therefore, this emphasizes the need to focus on improving the power density for this high energy electrode material in the future.

■ CATHODE MATERIALS

Conventional NICs employ capacitor-type cathode electrodes as the reaction mechanism involved in anion storage through nonfaradic surface adsorption/desorption.¹⁶ Highly porous activated carbon is the eminent choice for use in a cathode because of its high electrical conductivity, high surface area, chemical stability, and low cost. The large number of pores in carbon are the active sites for anion storage during the NIC charge-discharge process. Although activated carbon produced from coal/coke has a high surface area, it exhibits a poor rate performance due to ion-diffusional losses originating from tortuous pore networks (bottleneck pores).¹⁶ The energy retention of NICs employing an activated carbon cathode is extremely low under high power conditions.⁸³

Biomass-derived porous carbons have been proposed as a better cathode for NICs. Unlike activated carbon, biomass-derived porous carbon utilizes waste biomass resources for production.⁸⁴ A simple carbonization followed by a chemical activation technique (e.g., KOH, ZnCl₂, and H₃PO₄) can produce high surface area carbon with properties similar to those of active carbon. Activated carbon from various biomass resources, such as cinnamon sticks, peanut shells, cotton stalks, garlic, and corn silk, has been studied for use as cathodes for NICs.^{85–87} Biomass-derived porous carbon exhibits a discharge capacity (>60 mAh g⁻¹) higher than that of activated carbon (<45 mAh g⁻¹) and a better rate behavior. Moreover, the textural and surface properties of the cathodes, such as the surface area, surface functionalities, and porosity of the biomass-derived carbon, can be easily tuned to improve the capacity and rate capability of the cathode, without compromising the volumetric energy density.

More recently, a new class of nanocarbons, such as graphene, carbon nanotubes, carbon nanosheets with zeolite-derived carbon, ordered mesoporous carbon, and carbon nanofibers, have been studied as cathodes for NICs.^{18,22,88} The pores of 2D/3D structured carbon can be quickly accessed by anions in the electrolyte, thereby reducing the ion transport distance. Although the capacity of these 2D/3D structured cathodes is lower than that of the activated carbon owing to the low surface area, the rate capability is remarkably higher than that of activated carbon and biomass-derived carbon cathodes. Thus, the energy retention of NICs under high power conditions has been significantly improved with a nanocarbon cathode. The NIC based on the NaTi₂(PO₄)₃/graphene anode 2D graphene nanosheet cathode showed an energy density of ~80 Wh kg⁻¹ and a very high power density 8 kW kg⁻¹, much higher than that of activated carbon and the biomass-derived carbon cathode. The enhanced charge transfer kinetics and reduced interfacial resistance in the high-performing graphene cathode pushed the power limits of NICs to higher levels. Increasing the accessible surface area of the graphene cathode can simultaneously increase the capacity of the cathode and can further help to improve the energy retention at higher current rates. The recent strategy involves engineering the surface functionalities and surface defects of the nanocarbon cathode with single or multiple heteroatoms (N, S, B, F, O) to increase the surface utilization and shorten the diffusion pathways of electrons and anions.¹⁸ The heteroatom-enriched carbon cathode shows improved wettability with the organic electrode, thereby reducing the interface resistance during ion adsorption.⁸⁹ Such a heteroatom-doped nanocarbon cathode delivers the highest capacity and rate performance in a carbon-based cathode and is the most eminent cathode for future studies. Moreover, the power density of NICs employing such heteroatom-doped nanocarbon cathodes is far beyond (>20 kW kg⁻¹) the performance of EDLCs employing activated carbon and biomass carbon electrodes. In addition to a carbon-based cathode, metal oxides, polymers, and MXene compounds have also been utilized as cathodes for NICs and will be described in another section.

■ EMERGING MATERIALS: PSEUDOCAPACITIVE ELECTRODES

Pseudocapacitive charge storage is known for its rapid ion-storage kinetics, and electrode materials with pseudocapacitive storage are gaining attention for use in NICs. Unlike a bulk

sluggish intercalation process, pseudocapacitive electrodes utilize a surface redox to undergo fast kinetics. Fast kinetics combined with a higher gravimetric capacity can make them significantly superior to EDLCs. In addition, pseudocapacitive electrodes exhibit a linear charge–discharge profile similar to that of EDLCs. The sluggish ion kinetics with large-sized Na⁺ ions can be resolved by utilizing a pseudocapacitive electrode material. The pseudocapacitance is an intrinsic property of certain electrodes (RuO₂, MnO₂, and Nb₂O₅) but is extrinsic to other battery electrodes. Faradaic battery electrode materials undergo a pseudocapacitance-type charge storage with a smaller particle size and large surface area. The disappearance of redox peaks and plateaus during electrochemical characterization have been noted from several electrode materials when bringing the particle size from the bulk to the nanolevel. Using nanosized particles with a large surface area can significantly reduce the diffusion length of the ions into the electrode, thereby achieving high kinetics. However, the contribution from the bulk intercalation and surface pseudocapacitance should be clearly differentiated. Several metal oxides, sulfides, and metal-based anodes and cathodes were demonstrated with pseudocapacitance sodium-ion storage with a nanosized architecture.

Single-crystal-like anatase TiO₂ mesocages anchored on graphene showed a fast pseudocapacitive-type sodium-ion storage behavior with high reversibility and negligible degradation.⁹⁰ Approximately 73% of the charge storage is attributed to the capacitive-type Na⁺-ion storage in the TiO₂ mesocages. The capacity obtained by TiO₂ mesocages at a high rate (>100 mAh g⁻¹ at 20 °C) is far beyond the conventional Na⁺-ion storage in bulk-type TiO₂. The NIC studied using a TiO₂ mesocage anode and an AC cathode showed an energy density of 64.2 Wh kg⁻¹ and a maximum power density of 1357 W kg⁻¹, along with an ultralong stability of 90% retention after 10,000 cycles. Designing a nanoarchitecture anode is extremely crucial to realizing ultrafast sodium-ion storage. Coupling the nanoarchitecture with a high electronic conductive nanocarbon support will minimize the sodium diffusion length and electron transport path while maximizing the surface charge storage.

Similarly, NICs based on nanoarchitecture metal oxide anodes exhibited a high pseudocapacitive sodium-ion storage, with Na₂Ti₃O₇@CNT coaxial nanocables (52.7% contribution), MoP nanograins (75% contribution), N-doped porous carbon embedded with ultrasmall titanium oxynitride nanoparticles (76% contribution), sub-10 nm SnO₂ nanocrystals (86% contribution), 2D mesoporous carbon@TiO₂@carbon vertical heterostructures (96.4% contribution), and FeVO₄·0.6H₂O nanowires (96% contribution) and showed a remarkable energy retention under high power conditions.^{91–98} Another strategy to improve the pseudocapacitance is increasing the layer spacing in an oxide cathode. Enlarged interlayers with a stabilized layer structure can facilitate facile ion diffusion to achieve an excellent rate behavior and stability. The pyridine-V₂O₅·*n*H₂O nanowires exhibited a large pseudocapacitive behavior (78%) and an excellent rate capability considerably higher than that of a bulk architecture.⁹⁹ The NIC showed a maximum energy density of 96 Wh kg⁻¹ and a power density of 14 kW kg⁻¹, which is considerably higher than those of intercalation-based battery electrodes. The interlayer water molecule in the structure led to a “shielding effect”, which facilitated the fast solid-state diffusion of Na⁺ ions, leading to enhanced kinetics. Similar strategies in Fe–V–

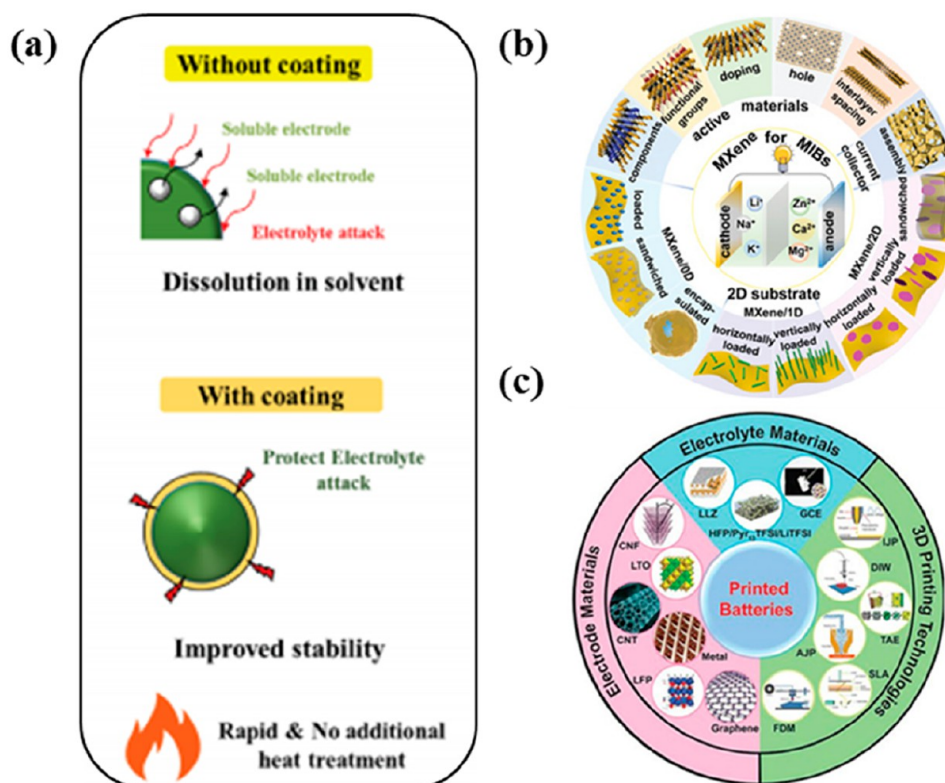


Figure 7. Several design strategies for emerging materials: (a) organic electrodes, (b) MXenes, and (c) flexible devices. Reprinted with permission ref 108, 134, and 135. Copyright 2020 Wiley.

O nanosheets, birnessite sodium manganese dioxide ($\text{Na}_0.77\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$) showed promising reaction kinetics.^{100,101} Although the initial energy density of NICs employing pseudocapacitance electrodes is slightly lower than the intercalation in alloy-type anodes, the kinetics at a high rate are far superior in the latter.

Such a fast pseudocapacitance and fast ion diffusion are observed in metal sulfides and binary metal sulfide anodes. The tailoring of sulfide-based anodes to ultrathin nanostructures can render a fast surface-dominated redox reaction in sulfide anodes. Several tailored nanostructures, such as WS_2 nanosheets (58% contribution), layer-by-layer stacked VS_2 nanosheets (69% contribution), few layered SnS_2 (75% contribution), $\text{Co}_9\text{S}_8/\text{ZnS}$ nanocrystals in hollow N-doped carbon nanosheets (90.3% contribution), MnCo_2S_4 Nanourchin (94.1% contribution), and SnS nanohoneycomb (95% contribution), have delivered a remarkably higher pseudocapacitance than their oxide counterparts.^{12,94,102–105} Sulfide anodes possess a larger discharge capacity than their oxide counterparts in an NIB system, and thus the energy output of sulfide-based NICs is higher than that of oxide-based NICs. An electrode material with a nanosized 3D architecture, high electronic conductivity, and large electrode–electrolyte contact area exhibits a larger pseudocapacitance than bulk-sized electrodes. An architecture that effectively shortens the ion-diffusion length can potentially improve the pseudocapacitive response of the electrode, thereby helping to achieve a high-rate capability.

Emerging Systems: Organic Electrodes. Apart from carbons, intercalation, and alloy-type electrodes, there are a wide range of materials that have been studied for NIC applications. Organic electrodes are one such system that have

gained significant attention owing to their sustainability and eco-friendliness. Unlike transition metal chemistry in conventional electrodes, organic electrodes take advantage of light elements, such as C, H, O, N, and S. Organic molecules are infinite resources and are widely available from natural resources. Moreover, organic electrodes have a high structural stability and wide chemical diversity, thereby providing a high capacity through simple redox reactions. Organic electrodes in NIBs have recently outperformed several inorganic electrodes in terms of energy, power, and cycle life. Consequently, using such green electrodes in NICs can result in a “green” output and highly “eco-friendly” energy storage device. For instance, Ranjith and co-workers demonstrated an “organic sodium-ion capacitor” device by employing disodium rhodizonate (DSRH) as a sodium-ion host and biomass-derived carbon as a cathode. Organic NIC showed a similar work mechanism during the charge–discharge process; i.e., Na^+ ions are stored in DSRH through a rapid redox reaction between the sodium ions and carbonyl group in DSRH and a simultaneous ClO_4^- anion adsorption in the cathode. Generally, organic electrodes exhibits poor kinetics due to their low electronic conductivity. A morphology-dependent Na-ion storage in DSRH was studied, and a nanosized DSRH exhibited an ionic and electronic conductivity high than that of bulk micron-sized DSRH electrodes, which is beneficial for pseudocapacitive ion storage at high currents. Organic NIC showed a high energy density (87 Wh kg^{-1}), high power density (10 kW kg^{-1}), and a high cycle life (85% at 10,000 cycles), outperforming inorganic sodium hosts. A 4.2 V NIC based on a polyimide organic anode and a polyimide-derived porous carbon cathode showed maximum energy and power densities of 66 and 1200 W kg^{-1} , respectively, which are lower than those of a carbonyl-based

organic anode.¹⁰⁶ The high energy density in organic NICs depends significantly on the number of active redox sites that can efficiently store large numbers of sodium ions during the charge-storage process. A large number of organic electrodes based on C=O reactions (quinone, carboxylates, and imides), C=N reactions (Schiff bases and pteridine derivatives), and doping reactions (nitroxyl radicals, organometallics, and polymers) have been studied for NIBs.¹⁰⁷ Moreover, it is essential to choose an electrode with a high capacity to realize a high energy NIC.

A similar research group attempted to improve the eco-friendliness of an organic NIC device by replacing the activated carbon cathode with green polymers. They reported a new class of "all-organic sodium-ion capacitor" device by coupling perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCD) and redox-active polyaniline as an anode and a cathode, respectively. The reaction mechanism in this capacitor involves Na⁺ storage in PTCD through enolate ion reactions and ClO₄ storage in a PANI cathode through redox reactions. The presence of both reactions are confirmed through the shape profile of cyclic voltammetry and CD curves, which depicts the synergetic effect between the two charge-storage mechanisms. A high energy density and power density of ~95 Wh kg⁻¹ and 7 kW kg⁻¹, respectively, were noted in the capacitor device along with an ~89% energy retention after 5000 cycles. The low cyclability and low-rate capability of organic systems are due to their high solubility in organic electrolytes and their poor electronic conductivity, respectively. Eminent approaches include several strategies, such as the use of a composite with high surface area nanocarbons (CNTs, CMKs, or graphene) or of a suitable electrolyte and additives and the polymerization of smaller organic molecules. We have recently addressed the solubility and kinetics of organic electrodes through the atomic-level manipulation of organic electrode particles using an ultrathin metal oxide coating.¹⁰⁸ Uniform and precise coatings applying a gas-phase atomic layer deposition technique have increased the interphase stability and enhanced the Na-ion kinetics of organic electrodes in NIBs (Figure 7a). The metal oxides coated organic electrodes showed very high stability and low electrode solubility than uncoated organic electrodes.

Emerging Systems: MXenes. MXenes are a large family of 2D-transition metal carbides and nitrides, which were first proposed by Gogotsi and co-workers. MXenes are derived from a layered MAX phase (M_{n+1}AX_n), where M is a transition metal, A is a III or IV A-group element, and X is carbon and/or nitrogen, through a hydrofluoric acid (HF) etching process. Since their invention, MXenes have gained significant attention in electrochemical energy storage devices owing to their high electronic conductivity, hydrophilicity, and wide redox-active surface areas in anodic and cathodic regions. The storage mechanism involves both bulk intercalation into MXenes and a surface pseudocapacitance, and the ultrafast kinetics are highly effective over sluggish intercalation kinetics. Yamada and co-workers first studied MXenes for NIC applications using Ti₂CT_x as an anode and Na₂Fe₂(SO₄)₃ as a cathode.¹⁰⁹ The pseudocapacitive sodium-ion storage in a Ti₂CT_x anode with a large discharge capacity makes them a better candidate than expanded graphite and hard carbon. The 2.4 V NIC delivered a high energy density of 260 Wh kg⁻¹ at a high power of 1.4 kW kg⁻¹. However, the cycle life has been studied for only 100 cycles (4% energy loss) and warrants further investigation.

The pseudocapacitance properties of MXene anodes can be easily controlled based on the number of MXene layers and the type of terminal functional groups (-F, =O, -Cl, and -OH) in the MXenes.¹¹⁰ The layer restacking issues during the synthesis process can reduce the active electrochemical sites, reducing the electrochemical performance of MXenes. Several strategies, such as vertical alignment of the MXene layers, introducing a carbon/polymer surfactant as a spacer, and introducing holes through chemical etching, can efficiently overcome layer restacking and significantly improve the electrochemical performance (Figure 7b).¹¹¹ The introduction of surface terminal functional groups by modifying the synthesis procedure can improve the interlayer spacing, improving the kinetics of MXene electrodes. Wang and co-workers further tuned the pseudocapacitance storage in a Ti₃C₂ anode using a cation (Li⁺, Na⁺, K⁺) pillaring effect.¹¹² The cation pillaring in a Ti₃C₂ anode significantly increases the interlayer spacing of MXenes, positively influencing the reversible capacity, rate performance, and stability. The NIC assembled using a Na-pillared Ti₃C₂ anode and an activated carbon cathode delivered a high energy density (80.2 Wh kg⁻¹) and high power density (6172 W kg⁻¹), including an ultralong stability (78.4% after 15,000 cycles).

Gogotsi and co-workers introduced a novel, free-standing, bistacking strategy in MXenes (Ti₃C₂) through a vacuum filtration technique.¹¹³ This avoids the use of current collectors and binders, and NIC with activated carbon offered energy and power densities of 39 Wh kg⁻¹ and 1140 W kg⁻¹, respectively, under high mass loading conditions (6 mg cm⁻²). MXenes show a greater charge-storage behavior than activated carbon and graphene when employed as cathodes for NICs. The large interlayer spacing can offer excellent sites for cation/anion accommodation at high voltage. NICs assembled using a presodiated hard carbon anode and a V₂CT_x cathode offer a 3.5 V output voltage and a capacity of 50 mAh g⁻¹.¹¹⁴ Unlike fast pseudocapacitive ion storage in the anodic region, MXenes undergo a combination of diffusion-limited redox storage and pseudocapacitive storage in the cathodic region. The MXenes also offer an excellent pseudocapacitance under both high- and low-temperature conditions, performing better than EDLCs.¹¹⁰ However, the thermal stability of MXenes at high temperature depends on the chemical composition, type of transition metal, surface functionalities, and structure of the MXenes.¹¹⁵ The ions in the electrolyte can rapidly undergo redox reactions with surface functionalities of MXenes even under different working temperatures. A robust NIC capable of performing under harsh climate conditions can be realized using MXene electrodes.

Emerging Systems: Flexible Capacitors. The development of portable and wearable energy storage devices for next-generation flexible electronics, displays, medical devices, and electronic skin is gaining prominence. Such flexible devices based on NIC are gaining significant attention. The electrode and electrolyte used in such devices should be mechanically strong, lightweight, and low cost, with appropriate flexibility.¹¹⁶

A common strategy for realizing a flexible capacitor is growing the electrode materials on flexible and free-standing substrates, such as carbon cloth, carbon fiber, carbon monolith, metal foams, and graphene (Figure 7c). These approaches avoid the need for current collectors, binders, or conductive carbon, leading to an excellent volumetric performance. Commercial carbon fiber/cloth is directly used to grow various metal oxides and sulfides and has been studied for flexible NICs. TiO₂ nanorods grown on carbon fiber showed a high

energy density and power density of 73.8 Wh kg^{-1} and $13,750 \text{ W kg}^{-1}$, respectively, when coupled with carbon fiber cathodes.¹¹⁷ A similar strategy was employed to fabricate other Ti-based anodes ($\text{Na}_2\text{Ti}_2\text{O}_5$ and $\text{Na}_2\text{Ti}_3\text{O}_7$), and the flexible NICs delivered an excellent energy–power behavior.^{118,119} The operating voltage, charge–discharge shape profile during different bending conditions, coulombic efficiency, and stability of these flexible NICs are similar to those of conventional NICs. Flexible NICs based on Sb_2O_3 and a Sb_2S_3 anode grown over a carbon fiber cloth were studied by Lang and co-workers.¹²⁰ The Sb_2O_3 and Sb_2S_3 delivered a high energy density of 124 and 117 Wh kg^{-1} , respectively, stability for 4000 cycles, and an excellent performance retention under different bending conditions. Mesoporous orthorhombic Nb_2O_5 over carbon fiber rendered 60 kW kg^{-1} of energy at 55 Wh kg^{-1} of power, equivalent to volumetric energy and power densities of 11.2 mWh cm^{-3} and 5.4 W cm^{-3} , respectively.¹²¹

Other novel 3D carbon-based substrates can provide an excellent electronic conductivity, and a long and continuous electron path was also studied for flexible NICs. Thus, Fan and co-workers fabricated arrays of mesoporous carbon nanosheets through the pyrolysis of 2D Co/Zn-MOF arrays that can efficiently function as flexible substrates for flexible NICs.¹⁷ The novel substrate combines a high surface area, heteroatom doping, excellent ion/electron conductivity, and an excellent mechanical flexibility, improving the energy–power–cycle life flexibility. Flexible arrays were encapsulated using a VO_2 anode and an NVP cathode, and the constructed flexible NIC rendered extraordinary gravimetric and volumetric energy (161 Wh kg^{-1} and 8.83 mWh cm^{-3}) as well as power behavior (24 kW kg^{-1} and 1.32 Wh cm^{-3}), outperforming carbon-cloth based devices. A similar research group introduced a mechanically robust and light porous carbon nanofiber utilizing a SiO_2 -etching approach. The flexible substrate demonstrated a nanoporous feature and can tolerate arbitrary bending and folding behaviors. This porous carbon serves as a 3D scaffold for developing a $\text{MoS}_2/\text{poly}(3,4\text{-ethylenedioxythiophene})$ core–shell anode, and the flexible NICs exhibited excellent stability, high-temperature performance, and high energy behavior. Importantly, the self-discharge rate ($\sim 15 \text{ mV h}^{-1}$) of NIC employing the 3D scaffolds is lower than that of the symmetric capacitors ($\sim 64 \text{ mV h}^{-1}$).¹²² A flexible NIC fabricated using a freestanding polyimide–graphene anode and a reduced graphene oxide cathode delivered an energy density of 55.5 and 21.5 Wh kg^{-1} at a power density of 395 and 3400 W kg^{-1} , respectively. These carbon-based electrodes are highly scalable, light in weight, and have a bendable nature.¹²³ Heterostructures of a Ti_3C_2 MXene/CNT composite without current collectors were realized through the electrostatic attraction between negatively charged Ti_3C_2 nanosheets and positively charged CNTs. These heterostructures can offer easy accessibility for electrolyte ions, excellent kinetics, and appropriate volumetric performance. The NICs employing a $\text{Ti}_3\text{C}_2/\text{CNT}$ anode and $\text{Na}_{0.44}\text{MnO}_2$ cathode showed a high volumetric discharge capacity of 286 mAh cm^{-3} .¹¹¹ Recently, MXene-based materials showed promise for use in flexible devices for energy storage, smart electronics, and healthcare applications.¹²⁴ MXenes can be functionalized to MXene inks without any additives and solvents and can be directly used for inkjet printing, flexographic printing, and roll-to-roll gravure printing. The solution-based MXenes can overcome the present difficulties of conductive inks such as poor conductivity

and high cost.¹²⁵ In addition, 3D printing technology was utilized for fabricating scalable nitrogen-doped MXene ($\text{N-Ti}_3\text{C}_2\text{T}_x$) scaffolds.¹²⁶ The active material ink can be directly 3D printed to form a free-standing architecture without a conventional current collector. A large areal mass loading of up to 15.2 mg cm^{-2} was 3D printed, and the NIC can harvest an areal energy and power density of 1.18 mWh cm^{-2} and 40.15 mW cm^{-2} , respectively. Such 3D printing is an eminent future strategy for the design of an energy storage system of any architecture.

Another strategy involves the design of a Na^+ -ion conducting gel polymer membrane as an electrolyte between a flexible anode and cathode.¹¹⁶ The Na^+ -ion conductivity of the electrolyte plays a crucial role in determining the performance of the sodium-ion hybrid capacitor. Kim and co-workers¹²⁷ have previously studied the effect of carbonate and ether-based electrolytes in NICs employing activated carbon and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. The ionic conductivity of the electrolyte was strongly influenced by the dielectric constant of the solvent. Also, they revealed that the oxidative stability of electrolyte, and the large number of free ions in the electrolyte will critically affect the kinetics and stability of NIC. Several polymers based on poly(vinylidene fluoride-co-hexafluoropropylene), poly(methyl methacrylate), polyacrylonitrile, and polydopamine have been utilized as Na^+ -ion conducting gel polymer electrolytes.¹²⁸ The polymer electrolyte membrane can provide an additional elasticity, flexibility, uniform sodium-ion flux, and safety to a flexible device.¹²⁹ The polymer membranes are known for their excellent stretchability and are capable of withstanding a huge amount of strain. Flexible NICs fabricated using a polymer gel electrolyte rendered an excellent bending characteristic and a superior stability over a conventional separator and liquid electrolyte. A flexible quasi-solid-state NIC based on TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ and carbon anodes employing a P(VDF-HFP) membrane were also studied, and the performance metrics of the devices are highly encouraging.^{33,119} The mass loading of the flexible devices should be high enough to ensure the high volumetric and areal energy–power behavior of the flexible/quasi-solid state NIC device. Owing to fast pseudocapacitive Na^+ storage, high mass loading and low graphene content, the quasi-solid-state NIC employing TiO_2 anode delivered an impressive volumetric energy and power density of $\sim 89 \text{ Wh L}^{-1}$ and $\sim 9.4 \text{ kW L}^{-1}$, respectively.¹³⁰

Emerging Systems: Synchrotron Tools for NHC.

Although the reaction mechanism of Na-ion storage electrode materials was intensely investigated utilizing X-ray synchrotron tools like in situ XRD, XANES, and EXAFS, the Na^+ -ion storage mechanism of the electrode materials were not widely investigated in the NHC application.^{131,132} Investigation of the composition anodes and cathodes and the composition of the SEI/CEI layer over the electrodes gave interesting clues about reaction mechanism in a hybrid-ion capacitor. Recently, Chen and co-workers utilized in situ XRD tool to investigate the storage mechanism of NIC employing porous NaBi anode, activated carbon cathode with NaPF_6 in diglyme as the electrolyte.¹³³ The results show a clear phase transition from NaBi to Na_3Bi during the charge process. However, a small amount of NaBi is observed in the NHC anode even when charged to a higher voltage of 3.5 V. The incomplete conversion of NaBi to Na_3Bi is due to kinetic effects in the fast charging hybrid capacitor device. The study emphasized the need for a high-capacity anode that efficiently stores Na^+

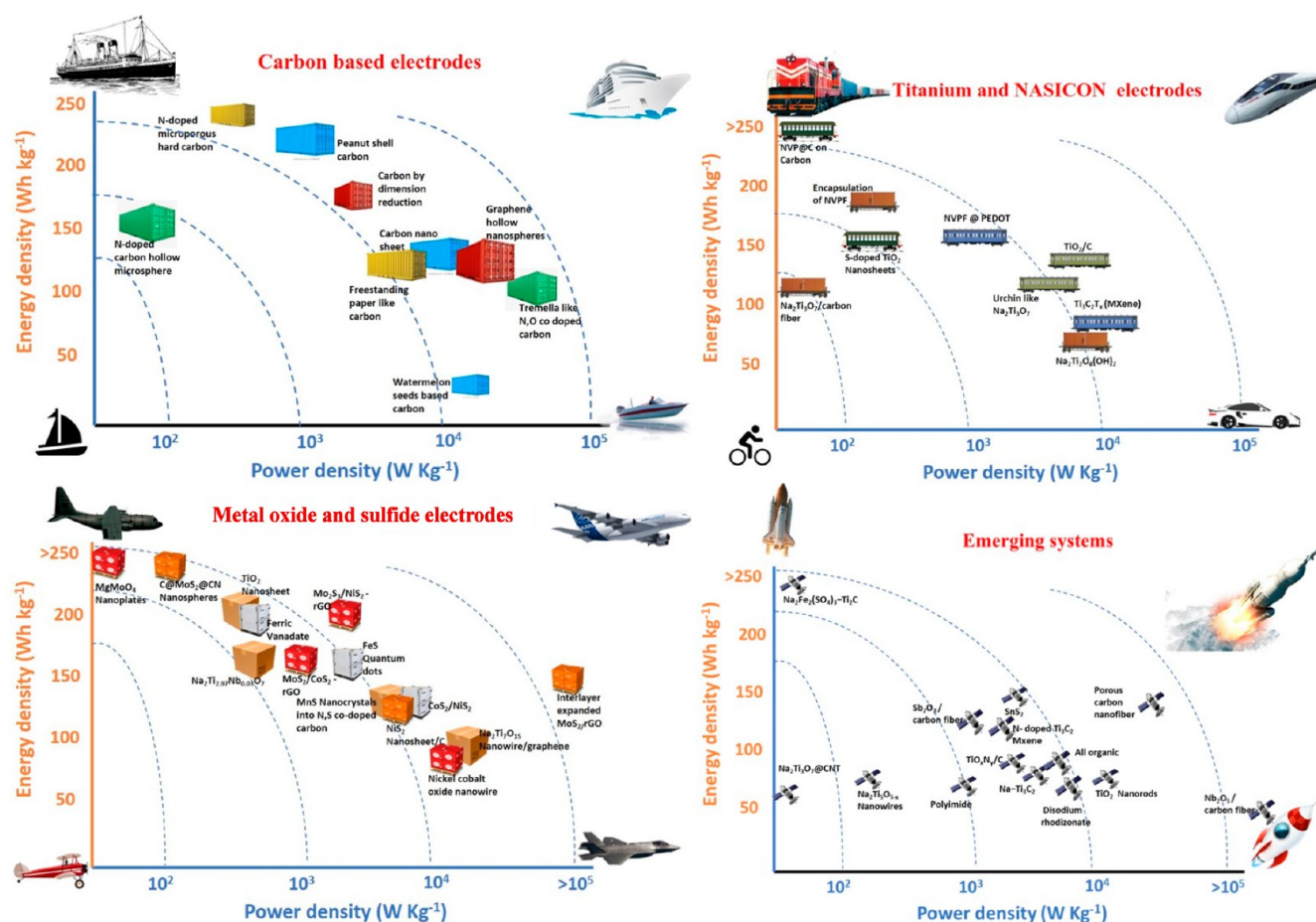


Figure 8. Ragone plot for various significant electrode materials in their category, such as carbon materials (top left), titanium and polyanion based (top right), metal oxide and sulfide-based electrodes (bottom left), and emerging electrode materials (bottom right).

ions even at high power conditions. The sluggish Na^+ -ion kinetics will lead to huge energy loss in NHC when tested in high power conditions. Upon consequent discharge, Na_3Bi converts to the Bi phase through two phase reactions ($\text{Na}_3\text{Bi} \rightarrow \text{NaBi} \rightarrow \text{Bi}$). Also, the authors revealed the formation of nanometer-sized SEI films through electron microscopy tools, and the thin SEI layer ensured the structural stability of hybrid ion capacitor system. The reversible anion (PF_6^-) absorption/desorption over the cathode was also clearly studied by elemental mappings and energy-dispersive X-ray spectroscopy patterns.

CONCLUSION AND OUTLOOK

NICs hold great promise for next-generation energy storage devices, benefiting from simultaneous high energy, high power, and long cycle life combination at low cost (Figure 8). Recent studies have shown the possibility of NIC devices performing beyond lithium analogues.

The performance metrics of NICs were realized through intercalation and metal-oxide-based electrodes during the initial development stage. However, research using conventional bulk-type intercalation and metal-oxide electrode materials is nearing saturation, and there is no room for further development. The future research must focus on newly emerging capacitor systems and materials for new NICs. Combining the merits of nanotechnology and advanced

nanocharacterization tools could elucidate next-generation hybrid devices. The following aspects suggest that new strategies could direct future research and development on NICs for realizing a superior device for use in next-generation energy storage devices.

- Research on carbon-based materials have found an important ranking in electrodes used for NICs. However, a kinetic mismatch between a sluggish intercalation type storage in an anode (hard carbon and graphite) and a fast surface adsorption type storage in a cathode (porous carbon) undermines the performance of NICs. To circumvent this mismatch, designing a 2D/3D nanostructured carbon is crucial. Investigating rationally designed carbon nanostructures that function as a bifunctional electrode (both as an anode and cathode) can boost the efficiency of NICs exponentially. Infiltrating hetero atoms into a carbon matrix and optimizing the electrolyte for improving the coulombic efficiency could further move the applications of carbonaceous materials in NICs. Investigating new strategies to overcome a tedious presodiation strategy during NIC fabrication should also be considered.
- Alloy-type anodes (metals, sulfides, and selenides) have demonstrated a higher energy density than metal oxides and intercalation type electrodes. However, a poor energy retention at a high rate and poor cycle life

retention originating from poor electron conductivity and large volume expansion undermine the performance. A rationally designed alloy type anode with a decreased particle size, nanodesign, and ultrathin carbon protective carbon will shorten the Na^+ diffusion path and reduce the volume expansion issues. For carbon anodes, new strategies to overcome the initial sodium-ion loss of NICs by employing alloy-type anodes should be efficiently engineered.

- Employing pseudocapacitive electrodes is an eminent strategy to improving the energy output of NICs under high power density conditions. However, the discharge capacity of pseudocapacitive electrodes is extremely smaller than that of carbon-based anodes and alloying-type anodes, thereby compromising the accuracy of the energy output of the NICs. The tuning of the crystalline structures, morphology, stoichiometry, and elemental valences of several compounds can deliver a high-performance NIC.
- MXenes are the newest material applied but have a significant potential for use in future energy storage devices. The physical and chemical properties of MXenes must be extensively studied before practical implementation. In particular, addressing the low initial coulombic efficiency and large irreversibility during the initial cycling will have substantial importance. Understanding the interface between electrolyte ions and MXene layer by utilizing sophisticated characterization tools could elucidate the ion storage principles.
- Organic electrodes are going to be a game changing electrode in future energy storage devices owing to their eco-friendliness and wide availability. Although organic-based capacitors have exhibited a similar performance as their inorganic counterparts, the power and stability of the devices require significant improvement. Addressing the kinetics and interface issues of organic electrodes using a nanocarbon composite, as well as ultrathin nanocoating strategies, could further enhance the power and cycle life of organic capacitor devices. Extending these strategies for low-voltage and high-capacity organic electrodes could induce the synergy of a high energy output and long cycle life.
- The rapid development of flexible electronics encourages further research on flexible and wearable energy storage systems, such as flexible batteries and capacitors. Future studies should focus on designing a new variety of flexible substrates, which are lightweight, with a highly porous structure and high flexibility, that can efficiently hold large amounts of active materials. Integrating the MXenes, pseudocapacitive electrodes, and alloy-type electrodes can synergistically produce a high performance in wearable devices. A high volumetric performance should always be considered in a flexible NIC. Furthermore, introducing new polymer/gel electrolytes with a high Na^+ conductivity (10^{-3} – 10^{-1} S cm^{-1}) and high thermal stability can elevate the safety of flexible NICs.
- Real-time characterization of sodium-ion hybrid capacitors utilizing several X-ray based synchrotron tools can give insights on improved kinetics in anode and cathode materials of NICs.

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Notes

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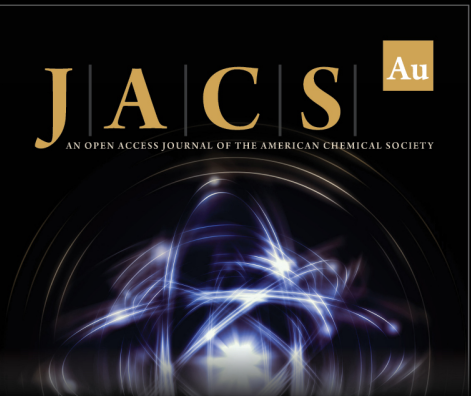
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