



Sodium-Ion-Based Hybrid Devices

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Abstract

The rapid growth of the population and the global economy has significantly increased the demand for energy consumption. To this end, batteries and electrochemical supercapacitors (ESCs) are recognized as the two most important types of electrochemical conversion devices in a matter of advances in energy storage. Therefore, a novel energy storage system has emerged combining the advantages of batteries and supercapacitors, the hybrid capacitors (HCs). Sodium-ion hybrid capacitors (SIHCs) are promising for large-scale electric energy storage benefiting from the low cost and the high abundance of sodium. SIHCs are generally composed of two electrodes for redox reactions: the anode is in battery form and cathode ion sorption in the ESCs. The big challenge for SIHC's large-scale expansion is the sluggish redox reaction kinetics of the fast-capacitive sorption in the capacitor-type electrode, which fails to match the battery-type electrode. In this regard, SIHCs face a big challenge in reaching high power and energy density, especially lacking suitable battery-type electrodes with fast redox responses. This chapter provides a brief introduction to the charge storage mechanism of the different energy storage systems and the experimental methods for the performance evaluation of SIHC devices. Additionally, insights into the recent studies of SIHCs systems are provided, focusing on materials design, electrochemical performance, and some aspects of the value market. Finally, some challenges and future perspectives on SIHC research are presented.

Keywords

Sodium-ion hybrid capacitors · SIHCs · Battery-type electrodes · Capacitive electrodes · Pseudocapacitance · Storage mechanism

Introduction

Energy storage systems have gained a lot of attention in scientific research and manufacturing consumer products in various areas of industry. In addition to the industrial appeal, the search for new clean and renewable energy devices is driven by environmental concerns such as climate change and environmental pollution, for example. As a result, there is a very high demand for devices with high storage capacity and high stability day and night. In this scenario, electrochemical energy storage devices have gained huge attention because it provides a modular solution in worldwide applications. The main types of electrical storage devices are batteries and electrochemical capacitors (Dong et al. [2021](#)).

Batteries are devices based on redox reactions in electrodes and store energy through a Faradaic process. These devices produce high energy density but have low performance relative to power density. On the other hand, electrochemical capacitors have high power density (10 kW Kg^{-1}) and low energy density (in the range of 5 W h Kg^{-1}). Although their drawback, lithium-ion batteries (LIBs) and supercapacitors are still the most used power supply in electric vehicles, mobile electronics, energy recovery in subway trains, and so forth (Yuan et al. 2018). To overcome these drawbacks, hybrid supercapacitor (HSC) devices that include the characteristics of both (battery and supercapacitor) have emerged as an advanced electrochemical energy-storage system.

HSCs can simultaneously deliver a high energy and power density in a single device. The HSCs are devices composed of a battery-type electrode, usually is the anode, and a supercapacitor electrode, the cathode. In this configuration, the energy storage occurs in the capacitive cathode and battery-type anode. The electrical potential of the capacitor-type electrode is restricted by decomposition of the electrolyte, so the combination with battery-type anode with high capacity and low potential can provide high energy density (Shaikh et al. 2021).

Lithium-ion capacitors (LICs), based on activated carbon as cathode and nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the anode, were proposed as a hybrid device in 2001. The system shows expressive high energy density of over 20 W h kg^{-1} (Amatucci et al. 2001). Thenceforth, due to the electrochemical potential of the hybrid capacitor, sodium-ion has been proposed to replace lithium-ion. The limited lithium resource has driven the research on sodium-based systems since sodium is abundant and geographically available (Li et al. 2018a, b).

The sodium-ion hybrid capacitors (SIHCs) present similar physicochemical properties to LICs. However, the SIHC field is relatively young, while LICs are already being commercially employed (Dong et al. 2021). Most of the studies on SIHCs are in the laboratory stage and have focused on improving electrode materials. The main issue is the radius of Na^+ that is larger than Li^+ (1.02 vs. 0.76 \AA), which can lead to the sluggish kinetics of Na^+ intercalation into anode material (Wei et al. 2018). Therefore, developing new materials that act as anode and cathode with high electrochemical efficiency is essential.

This chapter aims to focus on covering recent studies on SIHC devices. Hence, this chapter is organized as follows. Section “[The Energy Storage Mechanism of Batteries, Supercapacitors, and Hybrid Devices](#)” presents a brief comparison between batteries, supercapacitors, and hybrid devices. The principal methods for the experimental evaluation of SIHC devices are presented and discussed in section “[Principles and Methods for Experimental Evaluation of SIHCs Devices](#)”. Section “[Recent Advances in na-Ion Hybrid Capacitor \(SIHC\) Materials](#)” brings the recent advances in cathode, anode, separators, and electrolyte materials used to build a SIHC device. The advantages and disadvantages of SIHC devices are described in section “[Advantages and Challenges of SIHC Devices](#)”. Finally, the future directions and challenges related to SIHC are presented in section “[Summary and Outlook](#)”.

The Energy Storage Mechanism of Batteries, Supercapacitors, and Hybrid Devices

Batteries

Batteries are efficient energy storage devices that transform chemical energy into electrical energy through oxidoreduction reactions. The general mechanism of batteries involves the electron transfer from anode to the cathode through the ion's conductor, the electrolyte, when in a discharge process. In the case of rechargeable devices, it is possible to charge the battery again; thus, the current flux is inverted. The ion conductor is often an aqueous or organic solvent where inorganic species, such as salts, bases, or acids, are dissolved to maintain ionic conductivity (Korthauer 2018).

Since the discovery of the primary battery by Alexander Volta around 1800 (Korthauer 2018), huge efforts have been made to improve its performance. Today, batteries based on lithium materials are the most effective devices widely employed in various portable electronic and hybrid electric vehicles.

Lithium battery is a type of rechargeable battery composed of anode, cathode, separator, and electrolyte. Usually, the anode is a carbon-based material; the cathode is an oxide like LiCoO_2 ; the separator is a polymeric-based material; the electrolyte is an organic solvent. The discharge mechanism of the lithium battery is based on the movement of lithium ions from the negative electrode to the positive electrode, and the charging step is the contrary movement. They have a high-energy density, low self-discharge, long life, and low maintenance costs (Korthauer 2018).

Although lithium batteries possess numerous benefits, there still are some drawbacks, including the low power density and limited supply of lithium resources, that limit their large-scale energy storage application. In addition, the high reactivity of lithium is another issue to be solved. These disadvantages make lithium battery being in constant development. Most researchers seek to improve the components to become batteries safe and more efficient (Linden 1995). In the last years, the sodium-ion battery has emerged as potential substitute for lithium owing to its low cost for production and abundance of sodium. Different researches have demonstrated the efficacy of sodium batteries (Rojo et al. 2018). However, it is a young technology and needs extensive development to improve its power density and stability.

Supercapacitors

Supercapacitors are efficient energy devices, as well as batteries. Supercapacitors are used in electric vehicles, hybrid electric vehicles, fuel cells, and electronic devices like volatile memory backups in PCs. The first supercapacitor production started in the 1950s of the twentieth century, with the first experiments between the 1950s and 1970s by Standard Oil of Ohio (Yassine and Fabris 2017) and US companies

General Electric (Yassine and Fabris 2017). Today, the supercapacitor can provide charge-discharge current in a range of tenths to hundredths of amperes and with capacity of several thousand Farads (Libich et al. 2018). Supercapacitors have been divided into three main categories according to the energy principle. The most common types of supercapacitors are electrical double-layer capacitors (EDLC) and pseudo-supercapacitors (Libich et al. 2018).

The EDLC is the most common type and represents the majority on the commercial market of supercapacitors nowadays. It comprises a dielectric layer on the electrode, using electrostatic interaction to accumulate energy in Helmholtz double layer at the interface between the surface of the electrolytes and electrodes (Libich et al. 2018).

Pseudo-supercapacitors, or faradaic supercapacitors, are less used compared to EDLC. Their characteristics are similar to batteries, but present low power density and cycling stability. The pseudo capacitance is an effect of fast and reversible faradaic reactions, but it can be energy storage from non-Faradaic storage (Libich et al. 2018). It is between an EDLC (purely double layer storage) and a battery (purely Faradaic storage). The pseudocapacitance involves redox reaction and energy through the double layer, resulting in faradaic current. The energy is represented by the energy of molecule bonds, not stored in the dielectric layer. The disadvantage is associated with their principle, where during charge and discharge, the electrodes degrade faster than the electrostatic principle. Both electrodes are made of manganese dioxide (MnO_2) or ruthenium oxide (RuO_2). The stability, cycling, charge efficiency, and extended response times on pseudo-supercapacitors are all lower than on EDLC (Zhou et al. 2018).

Another known type of supercapacitor is the battery-type supercapacitor, also called a hybrid supercapacitor or supercapattery.

Battery-Type Supercapacitors

Hybrid supercapacitors or asymmetric supercapacitors are another classification that has progressed vastly. They consist of combination of advantages present in batteries cells and traditional supercapacitors (Fig. 1). Hybrid supercapacitors achieve high energy density, due to battery-type electrodes, and high power density, due to the non-faradaic capacitive, and also present good cycling stability. In a hybrid supercapacitor, faradaic and electrical double-layer capacitance occurs simultaneously (Zhou et al. 2018).

The first lithium hybrid supercapacitor (LICs) was developed in 2001 (Amatucci et al. 2001). Although LICs have demonstrated excellent electrochemical performance, several works have put expressive efforts into discovering new materials to replace lithium due to their limited resource (Dong et al. 2021). As an alternative, potassium ion capacitors (KICs) and sodium-ion hybrid capacitors (SIHCs) have been explored (Shaikh et al. 2021).

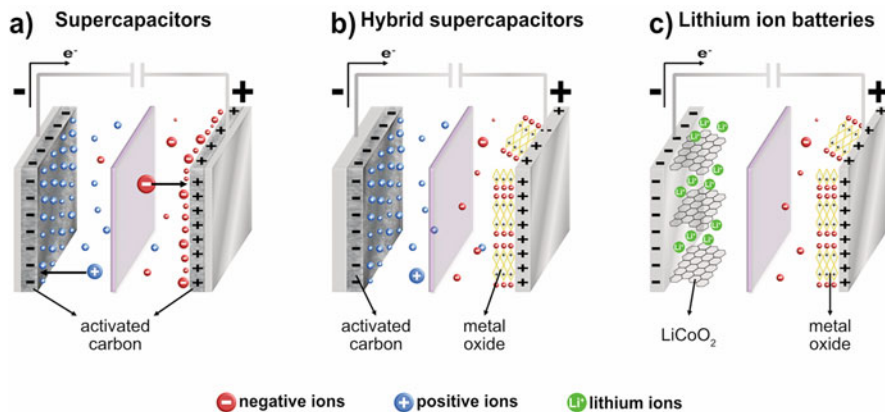


Fig. 1 Representative scheme of supercapacitors, SIHCs, and LIBs

SIHCs are emerged to replace lithium with large-scale energy storage applications due to their abundance and low cost. SIHCs were first developed in 2012 by Yin et al. (2012). It still is a young technology that remains on laboratory scale. The energy storage mechanism of SIHCs is similar to LICs. Basically, sodium-ions intercalated and deintercalated the electrodes through an organic electrolyte, converting chemical energy into electricity and vice versa. However, the mechanism is based on the cell configuration; thus, it is necessary to know the configuration to understand the mechanism. According to Dong et al. (Dong et al. 2021), the migration process of charge carrier is categorized into three types: (i) “accordion” mechanism; (ii) “rocking chair” mechanism; (iii) hybrid mechanism. The authors explain that in the first mechanism, the most common process, the hybrid capacitors are composed of a battery-type anode and a capacitive cathode, where cations and anions are separated in positive and negative electrodes during the charging process. In the second category, during the charge, the sodium migrated from the positive electrode (battery-type) and adsorbed on the negative electrode surface (capacitive) and moved contrary during the discharge. The last category is a combination of both mechanisms above.

Interestingly, one or both electrodes can be designed from capacitive and battery-type materials in this mechanism (Dong et al. 2021). In this way, in the charging process, cations (Na^+) are deintercalated from cathode to electrolyte and intercalated into the anode, while the capacitor-type materials in the cathode absorbed free anion from the electrolyte. On the contrary, the anions previously absorbed by the anode are released into the electrolyte during the discharging process to balance the cations deintercalated. At the same time, sodium-ions are inserted into the cathode to reestablish the system.

Principles and Methods for Experimental Evaluation of SIHCs Devices

The constant development leads to technological innovations being launched from time to time in the area. This fact shows the importance of having deeper knowledge of how these electrochemical systems work. For this, the experimental data must be compared for different HC systems.

But what experimental principles and methods should be used for these comparisons to be assertive? To answer this question, it is necessary to consider the aspects that need to be taken, such as components, energy storage, conversion mechanism, selection, and optimization of electrode materials. These factors can directly interfere with electrochemical performance and potential hybrid system applications.

Parameters such as power, performance, and voltage of HCs must be analyzed from specific methodologies. In this section, we will only briefly discuss some analytical techniques to determine such parameters. For deep understanding, other materials support the readers, including excellent books and reviews (Yu et al. 2013; Mathis et al. 2019).

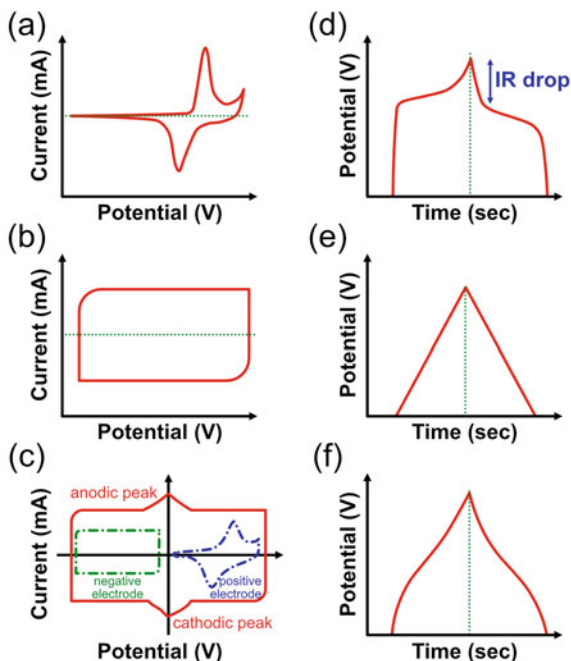
For SIHC characterization, the electrochemical cells are designed as two-electrode cells or as three-electrode cells. Two electrode cell is the ideal design to simulate the real operation condition for the capacitor. In a two-electrode system, the active material is deposited in negative and positive electrode surfaces. A two-electrode system can be classified as asymmetric or symmetric. In asymmetric systems, the negative and positive electrodes are composed of different materials, while in a symmetric capacitor, both electrodes are similar. Depending on the type of materials used as electrodes in the asymmetric system, we can classify the asymmetric system as a battery-type hybrid supercapacitor. In a three-electrode cell, the active material is deposited in only one electrode, known as a working electrode. The last system is more usual in academic research since it is a fast measurement that does not involve the full cell assembly (Yu et al. 2013).

Analytical techniques such as cyclic voltammetry (CV), charge-discharge (CD), and electrochemical impedance (EIS) are handy tools for characterizing electrochemical systems. They can provide valuable information for determining electrical efficiency and power (Feng et al. 2022).

Cyclic Voltammetry (CV)

CV is the first technique to comprehend the electrochemical system's reaction mechanisms, kinetics, and reversibility. It can be employed to analyze both two-electrode and three-electrode cell configurations. CV analysis provides important qualitative or quantitative information about capacitive or pseudocapacitive materials behavior. As mentioned before, the charge storage mechanism in a capacitive material is based on the ions' adsorption at the electrode/electrolyte interface. This mechanism, in particular, shows characteristic rectangular curve (Fig. 2b).

Fig. 2 Schematic illustration of the electrochemical characteristics of battery, capacitor, and hybrid capacitor represented by the cyclic voltammograms (a, b, and c, respectively) and galvanostatic charging and discharging curves (e, f, and g, respectively)



On the other hand, in the battery materials, the charge storage is based on the fast Faradaic reactions, exhibiting peak-shaped CVs (Fig. 2a). In a hybrid system, the contribution of both behaviors is observed, reflected in the CV curves (Fig. 2c). Several parameters can be obtained from CV curves. For instance, in a three-electrode system, the specific capacitance (C_{sp}) of the material can be determined by integration of CV curve, as shown in Eq. 1 (Yu et al. 2013; Chen 2017):

$$C_{sp}(\text{F/g}) = i/mv \quad (1)$$

where i is the current (A); m is the mass of active material (g); and v is voltage scan rate (V/s).

In contrast, for a two-electrode system, to calculate the cell capacitance is necessary to consider both electrodes, as two capacitances connect in series, expressed by Eq. 2:

$$\frac{1}{C_{cell}} = \frac{1}{m_+ C_{sp+}} + \frac{1}{m_- C_{sp-}} \quad (2)$$

where m_+ and C_{sp+} are, respectively, the mass and the specific capacitance of positive electrode; analogously, m_- and C_{sp-} are the mass and the specific capacitance of negative electrode. Thus, the specific capacitance of cell can be calculated by Eq. 3:

$$C_{sp,cell} = \frac{C_{cell}}{m_+ + m_-} \quad (3)$$

Considering a symmetrical cell, $m_+ = m_- = m$, the relation between the specific capacitance of electrodes and specific capacitance of cell can be expressed by reducing Eq. 4:

$$C_{sp,cell} (\text{F/g}) = \frac{C_{sp}}{4} \quad (4)$$

where C_{sp} is the capacitance per unit mass for one electrode. However, for asymmetric cell, the $m_+ \neq m_-$ and the capacitance of each electrode must be considered. In this case, the use of three-electrode system for its measurement is more indicated.

Kinetics and mechanism reactions can also be undertaken from CV method. For this, the CV curves are obtained at various scan rates. Further, the current obtained for each scan rate is collected, and a linear fit of \log_i against \log_ν is plotted, based on Eq. 5:

$$i = av^b \quad (5)$$

From the linear curve of $\log(i)$ versus $\log(v)$, it is possible to obtain the angular coefficient and, then, to classify the reaction mechanism. According to the reports, a b -value of 0.5 represents an ideal intercalation process, while a b -value of close to the unit is due to the capacitive process (Yu et al. 2013).

CV analyses have been carried out varying the cathode material and electrolyte concentrations. In addition, capacitance values can be calculated for each experimental variable, and data regarding ionic mobility can also be related to the results. The CV curves serve as the basis for identifying specific bands, where pseudo-capacitive characteristics are amplified in the electrodes. It is a standard behavior observed in supercapacitors and directly linked to good diffusion in the micropores of the electrode material (Chowdhury et al. 2021).

Charge and Discharge Analysis (CD)

The charge and discharge techniques are the most usual and reliable methods to determine a material's capacitance. From this methodology, it is also possible to evaluate the electrochemical system's cycle life and determine the power density and energy density. As well as CV analysis, CD analysis can be employed for both two- and three-electrode systems. Usually, the measurement is made keeping the current constant and evaluating the cell voltage as a function of time (charge or discharge) (Fig. 2d–f). In the same way, CD curves are characteristic for each mechanism reaction. The CD curve is highly linear for a capacitive mechanism (Fig. 2e). On the other hand, for a hybrid capacitor (a capacitive and faradaic mechanism), the CD

curve is slightly deviated from linearity (Fig. 2f). While, for purely Faradaic processes, the CD curves are ever nonlinear (Akinwolemiwa et al. 2015).

For material with Faradaic behavior, the charging process leads to a deviation of potential rising upward, while the discharge process leads to a reduction of potential downward. This potential difference is known as IR drop (Fig. 2d). Higher IR drop is related to the material's internal resistance, which reflects in their low energy density. For instance, Phattharasupakun et al. (Phattharasupakun et al. 2018) have determined the IR drop from CD curves from sodium-ion capacitor based on a highly porous carbon electrode derived from Jasmine rice. Significant reduction in IR drop was observed due to its low internal resistance. In another example, CD analyses were performed in the three frequency bands. Specific capacitance values were obtained about the current densities and calculated through the system charge and discharge data. The specific ratio of current density was obtained by generating plots of voltage drop versus each current density value. From calculations, series resistance values (ESR) were obtained (Chowdhury et al. 2021).

To calculate the specific capacitance C_{sp} from CD curves of three-electrode system, Eq. 6 is often employed (Liu et al. 2020a, b, c)

$$C_{sp} = \frac{i\Delta t}{m\Delta V} \quad (6)$$

where i is the applied charge or discharge current (A), Δt refers to the charge or discharging time (s), m represents the mass of the active material (g), and ΔV is the voltage change (V).

For two-electrode system, the specific capacitance C_{sp} for one electrode can be determined from Eq. 7 (Liu et al. 2020a, b, c)

$$C_{sp} = \frac{4 i \Delta t}{m \Delta V} \quad (7)$$

Other important parameters can also be evaluated from CD curves, the power density (P , W kg^{-1}), and the energy density (E , Wh kg^{-1}) for two-electrode system, according to Eq. 8 and 9, respectively (Chen et al. 2018):

$$E = \frac{C(\Delta V)^2}{2} \quad (8)$$

$$P = \frac{E}{\Delta t} \quad (9)$$

where C is the specific capacity of the device.

CV at low scan rates and CD analysis can also be used complementarily. For this purpose, different current densities were studied, and the energy and power densities were analyzed for each HC. The data from Hao et al. (2021), as an example, showed fine symmetry between the curves, which indicates good reversibility rate performance, especially in the SIHC system. The data reported superior performance of the

SIHC from Hao's work compared to other SIHC found in the literature. Information about the electric double layer's the mass exchange of the ions were also analyzed. Different operating voltage windows were evaluated, concluding that hybrid devices can operate above the water decomposition voltage, at voltage windows. This fact is due to the coupling of electrodes in pairs, and it is determined by CV or EIS (Hao et al. 2021). Finally, the number of SIHC cycles is presented, showing up to 84.9% capacitance retention after 10,000 cycles. Thus, Hao's work shows the use of basic analysis techniques to determine the efficiency of a SIHC system (Hao et al. 2021).

Cyclic Voltammetry and Galvanostatic Charge-Discharge analyses carried out at different current densities, provide accurate data on the global reactions taking place in the electrodes. Tests are performed by measuring the potential as a function of time under constant current. Other data obtained are about the diffusion coefficient of electroactive species. For this, experimental measurements are performed by varying the concentration of species and mathematical calculations with the Nernst equation (Hao et al. 2021).

Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful technique to evaluate the properties of hybrid capacitors at different frequencies. The analysis is made in an equilibrated state provides valuable information about the internal resistance and material behavior. The Nyquist plot is the most common way to represent the impedance data (Mathis et al. 2019). In the review of Mathis et al., a deep enlightenment is given by the authors to comprehend the EIS data to avoid misinterpretation.

Jiang et al. (2019) have provided a Nyquist curve of different electrodes for the sodium-ion capacitor. The paper shows a semicircle in the medium frequency region due to the charge transfer resistance and an oblique line in the low frequency. According to the authors, this linear slope region higher than the angle of 45° is characteristic of capacitive behavior.

EIS analysis was also performed for the most promising series resistance values (ESR). The magnitude of ESR is responsible for limiting the power and the energy performance of the electrochemical capacitor. The data led to combination of the internal resistance of the active material and the electrolyte's mass, indicating good electrode material performance, especially about its capacitive nature. For the device to be used in practical terms, Chowdhury and collaborators performed repeated charge-discharge cycles so that the stability of the cycles could be observed (Chowdhury et al. 2021).

It is concluded that CV, CD, and EIS analysis alone do not bring much data. However, when used together, they lead to rich data and a reliable method for experimental evaluation of HC and SIHC devices (She et al. 2021). Thus, these analyzes can be used as the basis for any experimental evaluation methodology and can be used to compare different devices, such as batteries, capacitors, super-capacitors, and hybrid systems.

Others

Complementary analyses can enrich the characterization of systems and further study the variables involved in work on the development of HCs and SIHCs. Understanding the storage mechanism of SIHCs to improve the efficiency of the component materials is highly necessary. In situ analysis, including in situ nuclear magnetic resonance spectroscopy, in situ infrared spectroscopy, in situ X-ray diffraction, and electrochemical quartz crystal microbalance, has been also explored. These techniques provide complementary data to understand the charge-discharge process and the interaction between the electrode and moieties present on the electrolyte as a function of applied voltage (Pal et al. 2021).

Computational simulations can also elucidate dynamic electrochemistry and simulate thermodynamic and efficiency data (Murugesan et al. 2021). But note, these simulations are not simple as they involve electrochemical, electrical, mechanical, and thermal parameters. They lead to a mathematical study that relates non-linear partial differential equations and reaches high degree of complexity (Murugesan et al. 2021). The ideal is to use experimental data that must be calibrated, together with computer simulation, which reduces the uncertainty of analyzing data from HC and SIHC systems (Murugesan et al. 2021).

The correct assessment of the factors involved in the systems can contribute to scientific advances in the storage field and indicate future perspectives on which paths scientific research should follow. In Fig. 3, the infographic contains a basic script about the main analytical methods for the experimental characterization of hybrid systems. The infographic also suggests complementary analyzes that can contribute to the evaluation of systems, especially considering the study of dynamic electrochemistry. In addition, it suggests interface analyses that can help, in detail, the elucidation of HC and SIHC systems. The infographic also summarizes areas that can be correlated during experimental studies and in the production of evaluation methods for SIHC devices.

Finally, Fig. 3 gives clear suggestions of what analyses should be carried out so that experimental methodologies can be validated and that complete characterization of SIHC systems is possible. It is also essential that different areas of knowledge are addressed and related so that comparisons between hybrid systems are assertive and comprehensive.

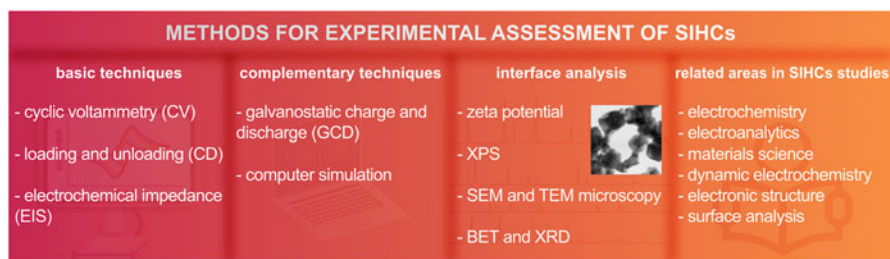


Fig. 3 Experimental assessment techniques for SIHCs and correlated areas in the study

Recent Advances in Na-Ion Hybrid Capacitor (SIHC) Materials

SIHC devices are composed of four components: electrodes, electrolytes, separator, and current separator, as shown in Fig. 4. The materials used to produce these components affect the energy storage mechanism and the performance of the hybrid capacitor. For hybrid capacitors, ion diffusion and charge transfer are the main energy storage ways. Thus, improving the materials for better electronic conductivity and ionic diffusivity is often the focus of researchers. Accordingly, this section is dedicated to discussing the recent advances in this area, concentrating on the advanced materials to design electrodes, electrolytes, and separators.

Electrodes

SIHCs are composed of two electrodes, cathode (as positive electrode) and anode (as negative electrode). The most common configuration of SIHC devices employs capacitive material as cathode and battery-type materials as the anode. In the

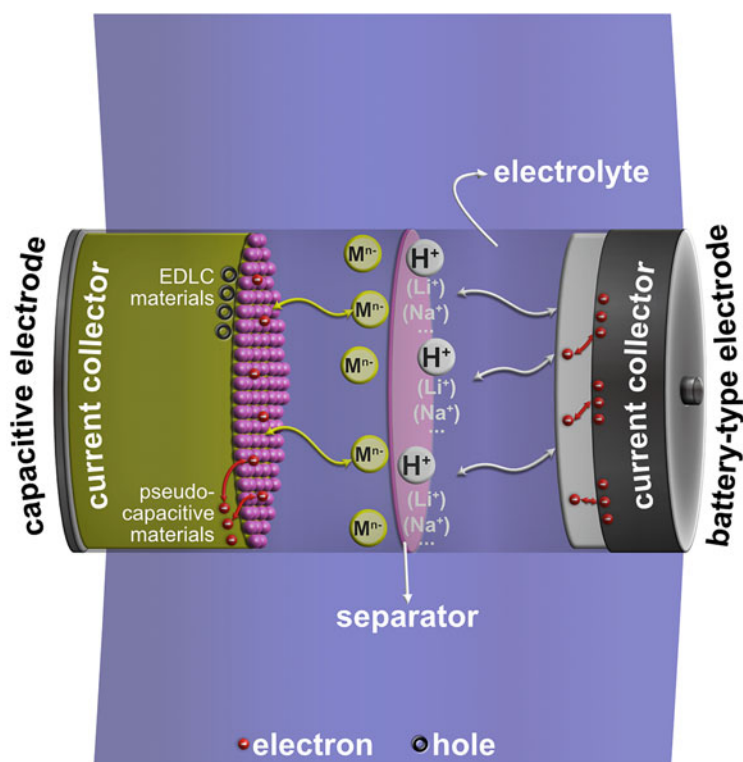


Fig. 4 General energy storage mechanism and device structure of SIHCs

capacitive cathode, the energy storage is based on the physical adsorption at the electrode/electrolyte interface. However, the anode suffers from the sluggish diffusion of sodium-ion that does not match the cathode electrode's fast sorption coming from the supercapacitors (Li et al. 2018a, b). In this way, researches for anode electrodes that improve energy density from the battery that presents a fast response and cyclability are highly desirable.

In another configuration, not most usual, the capacitive material is employed as anode and battery-type materials as cathode. This type of configuration is an alternative to overcome the electrolyte concentration fluctuation during the charge and discharge process (Wang et al. 2021).

The difference in potentials between the anode and cathode is responsible for the battery's output voltage. Thus, the in-depth study of materials for anode and cathode is extremely indispensable for the development of SIHCs. Hard carbon was successfully applied and demonstrated comparable performance to graphite. On the other hand, the development of cathodes is still at slow pace because an ideal cathode must have the following properties for practicality: (i) the ability to host alkaline ions, that is, high specific capacity; (ii) high redox potential; (iii) long service life, that is, the cathode material must not lose its structural integrity during cycles; (iv) high electronic conductivity in addition to high diffusion coefficient for Na^+ ions; (v) high thermal as well as chemical stability in addition to being compatible with electrolytes; and (iv) be easily obtainable, cheap, and non-toxic (Liu et al. 2020a, b, c).

Positive Electrode (Cathode)

Cathode is an important component for SIHCs. Numerous materials have been studied for use as cathode electrode. Some requirements for cathode materials are necessary to have high-performance hybrid capacitor. Among requirements are the compatibility with the electrolyte, high energy density, low cost, conductivity, and nonflammability (Linden 1995).

As mentioned in the above section, the most common SIHCs are composed of battery-type anode and capacitive cathode. The main capacitive materials are those based on carbon. Different carbon materials have been explored due to their large specific surface area and porosity structure, allowing high adsorption and fast ion/electron transportation. High adsorption is very important for cathode material to deliver high energy density for the electrochemical device (Wang et al. 2021).

Among the numerous studies, activated carbon with large specific surface area and adjustable pore structure has demonstrated high potential as cathode for SIHCs. For example, activated nitrogen-doped carbon nanosheets (NCNs) with high surface area ($1718 \text{ m}^2 \text{ g}^{-1}$) have been used as cathode for SIHCs by Li et al. (2018a, b). The NCNs were first prepared by hydrothermal method followed by precarbonization at $600 \text{ }^\circ\text{C}$ under the argon and then activated with KOH at $800 \text{ }^\circ\text{C}$ for 1 h. As for electrochemical performances, the individual capacitive analysis for cathode-activated carbon showed an expressive capacitance of 54 mAh g^{-1} at 0.1 A g^{-1} . Rectangular shape CV curve and linear CD profile are recognized, indicating capacitive behavior of electrode. After 6000 cycles at 10 A g^{-1} , the cathode kept

its performance with Coulombic efficiency of nearly 100%. These excellent results reveal superior adsorption-desorption process. Besides, a hybrid device was constructed using battery-type anode material (Fe_{1-x}S), and it demonstrated excellent electrochemical activity. Energy density of 88 Wh kg^{-1} , power density of $11,500 \text{ W kg}^{-1}$, and 93% capacity retention after 9000 cycles were obtained.

In another work, Wei et al. (Wei et al. 2017) have designed a SIHC device using commercial activated carbon as cathode and $\text{NaTi}_2(\text{PO}_4)_3$ mesocrystals as the anode. The activated carbon proved to be highly active material for adsorption/desorption of ClO_4^- and sodium storage. Consequently, the SIHC system delivers energy density of 56 Wh kg^{-1} at power density of 39 W kg^{-1} , supporting 20,000 cycles of charge-discharge without degradation. Other examples of activated carbon used as cathode for SIHCs include commercial activated carbon (Li et al. 2020), commercial microporous carbon fiber (Kang et al. 2019), and 3D framework activated carbon (Hu et al. 2021). All SIHC devices have shown expressive electrochemical performance.

Activated carbon nanomaterials have also been employed to design cathode and anode electrodes for SIHCs. Ding et al. (2015) used peanut shell and separated it into two parts to produce the carbon electrodes. The inner shell, composed primarily of lignin, was used to produce the anode (peanut shell ordered carbon – PSOC) due to its ability to form highly inter-dilated graphene layers that facilitate the sodium intercalation. In contrast, the cellulose-rich outer shell is an ideal precursor for nanosheets with high adsorption capacity as cathode (peanut shell nanosheet carbon – PSNC). According to the electrochemical tests, PSNC delivers specific capacity of 161 mAhg^{-1} at 0.1 A g^{-1} , while SIHC device provides energy density of 60 Wh kg^{-1} at power density of $34,000 \text{ W kg}^{-1}$, at 65°C . In addition, the hybrid device achieved 72% capacity retention after 10,000 cycles at 6.4 Ag^{-1} .

In the same way, a SIHC device was built with polyimide-derived activated carbon as cathode and polyimide as the anode (Zhao et al. 2018). Polyimide (polymer containing a large amount of imide groups) was used for preparing highly porous carbon. The authors reported a sheet-like carbon with high surface area ($1302 \text{ m}^2 \text{ g}^{-1}$) and functional groups on its surface. The activated carbon-based cathode's CV curves and CD profiles presented slight deviation of capacitive behavior due to its surface defects and functional groups that contribute to pseudocapacitance. However, major capacitive contribution has been succeeded. When applied as cathode in SIHC, the system delivered energy density of 66 Wh kg^{-1} at power density of 196 W kg^{-1} , operating at 4.2 V, showing fast adsorption/desorption kinetics and good reversibility of the activated carbon.

Biomass is an excellent carbon precursor. It is rich in carbon and presents various heteroatoms, including N, S, and P, that contribute to excellent electrochemical properties of the carbon's materials (Gong et al. 2017). Also, transforming biomass waste into carbon nanomaterials is a sustainable way to add value to products. For instance, Ramakrishnan et al. (Ramakrishnan et al. 2018) reported the synthesis of activated carbon derived from goat hair. The electrochemical test noted purely capacitive behavior, with maximum capacitance of 256 F g^{-1} at 0.02 A g^{-1} . The excellent performance of the activated carbon cathode was dedicated to the high specific surface area ($2042 \text{ m}^2 \text{ g}^{-1}$) and porous structure that facilitates ion

adsorption/desorption. Additionally, the hybrid device assembled using the molybdenum oxide and reduced graphene oxide ($\text{MoO}_2@\text{rGO}$), as anode, exhibits capacitance of 75 F g^{-1} at 0.02 A g^{-1} and energy density of 79 W h kg^{-1} at power density of 95 W kg^{-1} .

Garlic is another biomass source used to prepare carbon materials to act as electrodes for SIHCs. In their work, Liu et al. (2019) designed porous carbon as cathode and hard carbon as anode using the same biomass source. The porous carbon was obtained from KOH activation and carbonization methods. The resultant porous carbon shows high surface area ($1682 \text{ m}^2 \text{ g}^{-1}$) and delivered superior capacitance (152 mAhg^{-1} at 0.05 A g^{-1}). The hybrid device exhibited remarkable energy density of 156 W h kg^{-1} at 355 W kg^{-1} , providing 73% of capacitance retention after 10,000 cycles.

Similarly, Zhang et al. (2020) employed bacterial cellulose as carbon precursor in SIHCs. Here, both anode and cathode were constructed with identical hierarchical micropore-mesopore networks. The CV curves of the cathode exhibited dominant electric double layer with minor pseudocapacitance behavior, with relatively high capacitance of 115 F g^{-1} at 0.1 A g^{-1} . Besides, SIHC device could deliver high energy density of 124 W h kg^{-1} at power density of 210 W kg^{-1} and high long cycle stability (Zhang et al. 2020).

A promising hollow carbon nanobelt-based cathode for highly efficient sodium-ion capacitor was designed by Cui et al. (2019). In such work, the authors produced through self-templated method hollow carbon nanobelts doped with N and S and used them as active material in cathode electrode. The functional groups on the carbon surface provided pseudocapacitive behavior besides capacitive ion adsorption. Both mechanisms were responsible for the high electrochemical performance of the SIHC device, an energy density of $250.35 \text{ W h kg}^{-1}$ at 676 W kg^{-1} . Moreover, the SIHC exhibited high stability after 10,000 cycles, keeping almost 100% of its capacity.

Usually, capacitive materials are responsible for the ion's absorption-desorption process, while battery-type materials are responsible for the Faradaic reaction process. Although capacitive-type cathode has demonstrated expressive electrochemical performance, the most common issue about this configuration device is the sluggish kinetics of sodium-ions, the main obstacle for sodium-ion storage. Additionally, sodium-ion capacitor devices require huge electrolytes to deliver high ionic conductivity during charging (Wu et al. 2019; Dong et al. 2021). Recently, novel type of configuration has emerged as an alternative to overcome the main issues with traditional hybrid capacitor. The new hybrid capacitor comprises battery-type cathode and capacitive anode, whose function is the inverse of traditional SIHCs. Alternatively, pseudocapacitive cathode can also be used (Wei et al. 2018).

Among several studies for the development of cathode materials, sodium transition metal oxides have been drawing attention from the scientific community due to their compact crystal structure and their similarity to Li transition metal oxides (Liu et al. 2021a, b). Na-based compounds, such as polyanion-type fluorophosphates, are the main materials explored as cathode for SIHCs, owing to their high structure allowing sodium-ion storage and transport. For example, Wu et al. (2019a, b) have

employed $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}@$ PEDOT and activated carbon as cathode and anode, respectively, to assemble a SIHC device. The CV curves of the cathode demonstrated the Na-ion intercalation/deintercalation mechanism with high rate capability. The author attributed the increasing charge-transfer reaction kinetic to the PEDOT with excellent conductivity. Moreover, the hybrid device demonstrated impressive performance compared to the traditional SIHCs, delivering high energy density (158 Wh kg^{-1} at 230 W kg^{-1}).

Likewise, battery-type cathode was constructed with $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}/\text{rGO}$ material for SIHCs without the pre-sodiation process. Pre-sodiation is an important step because it improves the stability and the energy density of SIHCs. However, in this work, Dong et al. (Dong et al. 2020) designed a hybrid capacitor composed of battery-type cathode and pseudocapacitive anode that delivered high energy density (88 Wh kg^{-1} at 95 W kg^{-1}) and larger cycling stability (5000 cycles) without any additional pre-sodiation step. As cathode, the material used was $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}/\text{rGO}$, while layered iron vanadate ultrathin nanosheets were employed as the anode to produce hybrid capacitor (Wei et al. 2021). In such work, the cathode deintercalated Na^+ ions to be stored at the anode during the charge, and in the discharge step, Na^+ ions move contrary. Here, no pre-sodiation step was necessary, and the hybrid device could reach high energy density of 126 Wh kg^{-1} at 91 W kg^{-1} and stability even after 9000 cycles.

In another work, Wei et al. (2018) demonstrated the remarkable electrochemical potential of layered ferric vanadate (Fe-V-O) nanosheets as cathode. Layered transition metal oxides (TMOs) have attracted considerable attention since they are promising materials with high capability for Na^+ intercalation. So, the Fe-V-O nanosheets displayed significant electrochemical performance. When assembled the hybrid device, maximum energy density of 194 Wh kg^{-1} and power density of 3942 W kg^{-1} was reached.

P2-type layered materials, like $\text{Na}_{0.66}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, have demonstrated high discharge capacity and rate performance for SIHC devices, however poor cyclic stability. To overcome the main drawback, Kaliyappan and Chen (Kaliyappan and Chen 2018) have put their efforts into designing P2-type material ($\text{Na}_{0.66}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2 - \text{NMNC}$) through the atomic layer deposition of Al_2O_3 . According to the authors, the Al_2O_3 coating reduces the sluggish reaction at the high current cathode density. Furthermore, the SIHC device has energy density of 63 Wh kg^{-1} at power density of 6.6 kW kg^{-1} .

Negative Electrode (Anode)

The anode is one of the key components to determine the performance of Na^+ hybrid capacitors. The negative electrode materials can have long-life cycling and high specific capacity. Both properties ensure the increased overall energy storage density of cells.

Carbon-based materials are good candidates for negative electrodes to SIHCs, due to simple preparation, high capacity, and good cycle stability (Wang et al. 2021). Besides that, carbon-based materials have abundant resources. Often, the materials are used to be amorphous carbon and graphite. However, for SIHCs, the graphite

does not make negative electrodes because it does not make intercalation reaction with ion Na^+ (Wang et al. 2021). In contrast, graphene is a good candidate for producing SIHC anode due to its physical and chemical properties (Wang et al. 2021).

Generally, carbon nanomaterials have been employed with Ti-based nanomaterials as negative electrodes. Ti-based electrodes for SIHCs possess excellent chemical stability, high theoretical capacity, low sodium-ion insertion potential, and low toxicity (Zhai et al. 2019). Unfortunately, this conductor presents poor electronic conductivity that results in poor electrochemical performance. Thus, carbon can improve electronic conductivity and reaction kinetics (Wasalathilake et al. 2020). In this regard, scientists have done efforts to tune the structures of materials. For example, some materials with low dimensional, hollow, and hierarchical nanostructures have been designed, which boosts electrochemical properties (Fang et al. 2019).

For example, Chen et al. (2018) have proposed a new material based on titanium oxynitride nanoparticles ($\text{TiO}_x\text{N}_y/\text{C}$) encapsulated into N-doped porous carbon. Here, the nanoparticles were produced and uniformly dispersed into carbon due to the hierarchical structure of the metal-organic framework (MOF) precursor. Meanwhile, high-porous carbon-based cathode was prepared by HF etching to remove the TiO_xN_y nanoparticles from carbon. Due to the nature of battery-type anode and capacitive cathode, SIHC device exhibited high-energy density of 80 Wh kg^{-1} , high power density of 4000 W kg^{-1} , and superior cycling performance. Recently, Chen et al. (2020) have designed anode materials based on $\text{NaTi}_2(\text{PO}_4)_3$ (NTP) coated with carbon. Ultrathin carbon layer coat on the NTP improves the limited electronic conductivity, accelerating Na^+ and electron transport kinetics. Thus, the SIHCs developed with $\text{NaTi}_2(\text{PO}_4)_3@\text{C}$ nanorods, and commercially activated carbon displayed significantly high power density of $\sim 9180.0 \text{ W kg}^{-1}$ at 10 A g^{-1} . In addition, high stability was reached after 7000 cycles, keeping $\sim 94.5\%$ of its capacity.

With the development of two-dimension materials, two-dimensional transition metal carbides (MXenes) have emerged in recent years as promising materials, as anodes for SIHCs. MXenes have been shown to be effective anode due to their large specific surface area, high electronic conductivity, and fast ion/electron transport. Additionally, MXenes are highly flexible and easy to be functionalized, allowing the design of many MXenes derivatives (Zhu et al. 2017). The most known MXenes are based on titanium carbide (Ti_3C_2). For instance, Kurra et al. (Kurra et al. 2018) have reported the performance of bi-stacked titanium carbide (MXene) as anode for SIHCs. In this work, $\text{Ti}_3\text{C}_2\text{T}_x$ ($d\text{-Ti}_3\text{C}_2\text{T}_x$) was employed as current collector and support for multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ particles, which were deposited by vacuum-assisted filtration. This strategy allows the design of anode electrode binder or conductive additive-free. In this way, the electrochemical performance was evaluated and confirmed pseudocapacitive behavior of the material. As SIHC device, bi-stacked MXene was employed with commercial activated carbon as cathode and the hybrid capacitor delivers energy density of 39 Wh kg^{-1} at 1C rate and 23 Wh kg^{-1} at power density of 1140 W kg^{-1} .

In another work, Ti_3C_2 MXenes were used to produce hybrid architecture based on TiO_2 nanoparticles supported on graphene (Wang et al. 2018). The authors oxidized Ti_3C_2 MXenes into Ti-peroxo gel through H_2O_2 addition. Then, TiO_2 gel was added into graphene oxide dispersion, sonicated by 5 min, frozen, and annealed at 500°C . The TiO_2 -rGO hybrid nanoarchitecture obtained was used as the anode, and polyaniline derived porous carbon as the cathode. Combining both structures resulted in high Na^+ charge storage device capable of delivering energy density of 94.7 Wh kg^{-1} operation at high voltage (4.0 V).

Similarly, Ti_2CT_x -MXene was transformed into M- TiO_2 , creating lattice defects and oxygen vacancies during the synthesis. Further, graphene oxide was used to provide high conductivity and consequently fast Na^+ diffusion. As the anode, the M- TiO_2 @rGO composite shows purely pseudocapacitive storage mechanism with high electrochemical efficiency. Moreover, M- TiO_2 @rGO composite was used with 3D hierarchical porous activated carbon (HPAC) as the cathode to fabricate sodium-ion capacitor. As result, the SIHC exhibited maximum energy of 101.2 Wh kg^{-1} and power density of $10,103.7 \text{ W kg}^{-1}$ (Fang et al. 2020).

Reduced graphene oxide (rGO) has also been used as skeleton to vanadium diselenide (VSe_2) flower growth by Wu et al. (Y. Wu et al. 2019). The strategy created by the authors used rGO layers to avoid the VSe_2 aggregation. The 2D flower nanostructure acts as efficient energy storage system capable of fast Na^+ ion diffusion. Also, graphene enhances electrical conductivity and provides abundant channels for ion diffusion. To evaluate the electrochemical performance as anode, the authors have constructed a full cell using activated carbon as cathode and carried out CV and CD analysis. As SIHC, the unique nanostructure delivered significant energy density (106 Wh kg^{-1}) at 125 W kg^{-1} , bringing new insights for synthesizing Na^+ ion insertion/extraction electrodes.

Layered materials have been widely employed in the energy storage field as promising anode electrode for SIHCs. The large interlayer spacing and high specific surface area allow the fast ion intercalation/deintercalation process. For example, titanates ($\text{Na}_2\text{Ti}_3\text{O}_7$) possess high theoretical capacity of 310 mAh g^{-1} and optimal conductivity favoring their application in SIHCs (Gao et al. 2018). In same work, Gao et al. (Gao et al. 2018) synthesized 1D nanostructured $\text{Na}_2\text{Ti}_3\text{O}_7$ by in situ grown on Ti foils to improve the energy density of these systems. SIHC device was assembled using hierarchical carbon nanosheets as cathode and proved to be an excellent strategy to reach energy density of 49.0 Wh kg^{-1} at the power density of 825 W kg^{-1} .

Another layered material that demonstrated great potential as anode for SIHCs is the molybdenum diselenide (MoSe_2). 2D sandwiched $\text{MoSe}_2/\text{TiO}_2-x/\text{graphene}$ was synthesized by Liu et al. (2020a, b, c) to improve the rate capability and cyclic stability of the SIHC device. The authors' main goal was to take advantage of the synergistic effect of different structures to improve the electrochemical performance of anode electrodes. Thus, graphene is desirable to enhance the sodiation/desodiation reaction kinetics, while the TiO_2-x layer secures the reversibility of the sodiation/desodiation process. As a result, the SIHC device could deliver a maximum energy density of 109 Wh kg^{-1} at the power density of 100 W kg^{-1} .

Battery-type nanomaterials have demonstrated potential as anode for SIHCs due to their rapid faradaic reaction and stable Na^+ ion intercalation/deintercalation structure. Sn_4P_3 , $\text{Na}_2\text{FeSiO}_4$, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, Nb_2O_5 , V_2O_5 , NiCo_2O_4 , TiO_2 , and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ are the most representative anode materials (Deng et al. 2020). Orthorhombic niobium oxide has attracted the great attention of researchers. It possesses large interplanar lattice spacing that allows fast Na^+ ion diffusion and rapid pseudo-capacitive response (Jin et al. 2021). However, as with most oxide materials, Nb_2O_5 has poor electrical conductivity, requiring its integration with carbon materials. In this way, She et al. (2018) have prepared a new hybrid anode based on Nb_2O_5 nanoparticles anchored on N-doped graphene by solvothermal methods followed by annealing. Here, besides conductive support, graphene restricts crystal growth and prevents nanoparticle aggregation. Thus, a novel SIHC device was constructed using commercially activated carbon as the cathode. The new device delivers energy density of 40.5 Wh kg^{-1} at 100 W kg^{-1} and good stability even after 5000 cycles. Although this is not a powerful result, the research opens new avenues to design a fast ion diffusion anode for SIHCs.

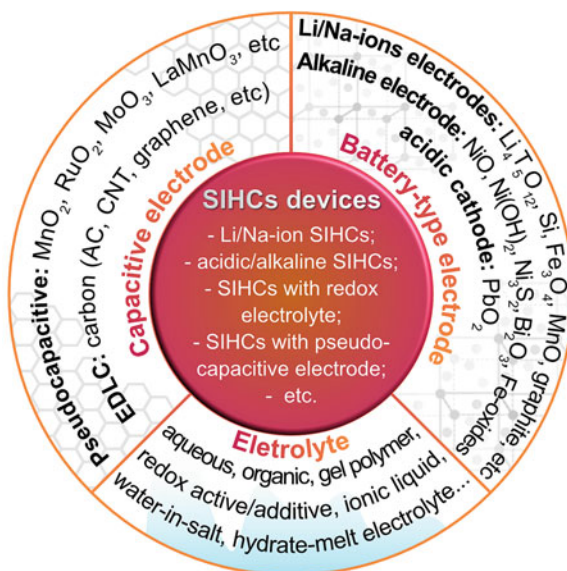
Electrolyte

The electrolyte is an essential part of SIHC as it can influence energy efficiency, capacity, and stability. For the electrolytes to affect all the aspects mentioned earlier in a positive way, they need to present some essential specifications related to high operating window, stability, low toxicity, and excellent ionic conductivity. Usually, SIHC electrolytes consist of sodium salt and solvent and occasionally need specific additives (Meng et al. 2020). However, we can cite some examples of electrolytes, such as organic, aqueous, nonaqueous, ionic liquid, and solid-state electrolytes (Meng et al. 2020).

Organic electrolytes have larger voltaic window than aqueous electrolytes, showing more operation than ionic liquid- and solid-state electrolytes (Meng et al. 2020). However, this type of electrolyte can present some problems such as flammability and toxicity. Aqueous electrolytes have high ionic conductivity and low resistance, which favors ions' transfer; however, they have low working voltage range. Typically, nonaqueous electrodes are quaternary ammonium salts dispersed in carbonates or acetonitrile (Glushenkov and Ellis 2018). Electrolytes based on ionic liquids have already shown good chemical stability, high conductivity, and high electrochemical resilience; in another way, due to its high cost, it is not attractive for large-scale commercial purposes. A solid-state electrolyte, such as polymers, can be an alternative to its ionic conducting medium that preserves high cycle numbers (Lamb and Burheim 2021). In this way, Liu et al. realized strong solid electrolyte interphase dependence in SIHCs (Liu et al. 2020a, b, c).

Polymer is an alternative as electrolyte for SIHCs. The polymer electrolyte presented excellent mechanical properties, and thin-film fabrication is considered easy. However, this type of electrolyte presents poor interfacial resistance and low electrical conductivity. Therefore, it is necessary to improve these properties. For

Fig. 5 Various types of SIHCs



example, the gel polymer electrolyte is a good candidate for SIHCs due to their unique structure (liquid electrolyte with polymer). This structure ensures cohesive properties (solids) and diffusive properties (liquids). Thereby, gel polymer electrolyte has good compatibility with electrodes, good ionic conductivity, and thermal stability (Yang et al. 2015).

Even Ganesan et al. (2021) analyzed hybrid mixed electrolytes. The mixture allowed to tune some properties to develop electrolytes to SIHCs with high stability caused by enhancing energy density and cyclic stability, for instance. Also, Zhang et al. (2018a, b) demonstrated the increase of the electrolyte concentration could enable high-energy density in SIHCs.

In summary, Fig. 5 shows the main electrodes and electrolytes for battery-supercapacitor hybrid devices, as above mentioned.

Separator

Separators are considered essential in energy storage devices as well as hybrid battery-supercapacitors, playing crucial role in determining the device's performance. Separators are the inactive fundamental and critical component, which comprises a porous membrane sandwiched between the anode and the cathode. The main function is to physically separate the cathode from the anode, to avoid electrical short circuits, and, at the same time, to provide a pathway for the transport of charge in the liquid electrolyte within the porous structure. These can be made of porous polymeric membrane and composite separator (Sun et al. 2014).

The separators do not involve any cell reactions; however, their properties and structure affect the SIHC performance. The materials regularly used are polypropylene (PP), poly (ethylene oxide) (PEO), glass fiber, and poly(vinylidene fluoride) (PVDF). However, it is necessary to develop new separators to improve the SIHC performance (Wang et al. 2020a, b).

Some interesting examples are demonstrated with the following recent works. Surendran et al. (Surendran et al. 2019) made a spongy sprout separator that demonstrated excellent chemical and mechanical stability even after 10,000 charge-discharge cycles. As shown by Zhang and collaborators, cellulose-based binders and separators for SIHCs are also explored (Zhang et al. 2018a, b).

Current Collector

Current collectors support active materials such as cathodes and anodes and connect the electrodes in external circuit. Recently, efforts have been made to improve energy density, charging, and discharging. One such factor is hardness, thickness, composition, and the coating layer (Yamada et al. 2020).

Carbon fibers are generally used as conductive current collector for electrode materials. However, these materials are expensive and demand complex calculations during the process, which limits their commercialization. Other carbon materials are well used as substitutes in these cases. For example, Wang et al. (Wang et al. 2020a, b) used commercial cotton cloth to produce the current collector. After hydrothermal treatment, Ni-Co hydroxy-carbonate nanowire arrays were applied on the core-shell-like structure. Finally, Ni-Co selenide nanowires/nickel-plated cotton cloth is formed. Ni et al. (2013) used graphite as current collector, which guaranteed the stability of the electrode in an H_2SO_4 environment. Thus, PbO_2 was deposited on the graphite substrate as anode electrode and activated carbon as cathode electrode. The capacity only decreased by 20% from the initial value after 3000 cycles.

Advantages and Challenges of SIHC Devices

Combining the capacitive and battery electrodes is a good choice for energy storage device construction. Alone, they make storage systems that perform well but come with some disadvantages. For instance, batteries have poor cycling life stability, and supercapacitors exhibit low energy density. However, bringing both together into a single simple device can be critical to increasing the performance and ensuring good characteristics needed for great energy storage devices such as long-life cycles and high power density and energy density.

Currently, the replacement of Li for another ion is a good alternative for the increase in the industrial production of storage devices with a lower cost. Low market values (\$135–165/ton Na_2CO_3) and the 2.3% abundance of Na in the Earth's crust have increasingly encouraged energy storage devices to replace the Li^+ (\$5000/

ton Li_2CO_3 and 0.0017% abundance). These ions have similar properties, so their replacement becomes more interesting (Feng et al. 2020).

The substitution of Li^+ ion by Na^+ ion is a good alternative for cheaper devices and large-scale production at industrial level. This process requires further research since the materials used as electrodes in Li^+ ion devices are not very favorable for harboring Na^+ ones. The materials commonly used for Li^+ ion exhibit low capacity and are considered inactive when related to the ionic mobility of Na^+ ion (Xu et al. 2022).

Regarding SIHCs, recent research shows that they have a combination of high capacity to store energy and high power combined with the merits of battery and capacitor. However, the development of SIHC has some challenges watching structure and performance. For example, there still is limited transfer rate caused by the low conductivity of materials with pseudocapacitance and the kinetic delay due to the low ionic diffusion rate of battery-type materials when subjected to high energy (Huang et al. 2018; Tie et al. 2019).

In this perspective, the materials used as anodes need to overcome the kinetic imbalance that happens between the electrodes. The materials whose the electrode is built need, necessarily, to exhibit suitability to store the Na^+ , since Na^+ has a larger radius (1.02 Å) than the radius of Li^+ ion (0.76 Å). In addition, the slow diffusion of ions into the anode and the low capacity exhibited by the cathode decreases the efficiency of SIHCs. However, these problems can be resolved using materials that exhibit rapid pseudocapacitance and high specific capability (Feng et al. 2020).

Additionally, the size of the Na^+ ion still causes structural problems for the electrodes. Because the ions migrate between the electrodes during redox reactions, the increase in the volume of the ionic species due to change of Li^+ by Na^+ can result in deterioration processes in the structure of the electrodes, reducing the electrochemical efficiency of the devices. Given the initial research stage on hybrid devices based on Na^+ ions, this is one of the main challenges to be studied and resolved in the near future (Liu et al. 2021a, b, c).

Summary and Outlook

With the current modernization of the world electric sector, renewable energy matrices and increasingly autonomous networks tend to use renewable energy matrices. As a result, the research field in hybrid capacitors (HCs) that combine advantages of batteries and supercapacitors has been expanded, and technological innovations in the area have been multiplied every year. In view of this fact, the latest advancement of sodium-ion hybrid capacitors (SIHCs), including the mechanism storage, the electrochemical characterization, electrode materials, and other components, were presented here. Based on the recent advances, SIHCs are promising for energy storage, benefiting from the low cost of sodium and its high abundance. However, it is still a young technology that needs more studies for large-scale applications. To date, many SIHC systems have still problems to solve, such as

low current density, low cycle stability, and limiting the use to only a few hundred cycles. Thus, future research needs to focus on the following points:

1. The main challenge about energy storage hybrid devices is the development of suitable materials (electrodes) that shows satisfactory performance since the power density, charge and discharge rate, life cycle, and other properties of hybrid devices are determined by the electrodes. Up to now, carbon materials are still dominating the research. As capacitive cathode electrodes, their intrinsic properties provide excellent ability to fast ions' adsorption. However, the specific capacity even remains insufficient. We have demonstrated that battery-type cathode has emerged as an alternative to overcome the main issue of the capacitive electrode. Still, this field's research is far away from the ideal goal. As the anode, carbon nanostructures can be used only or in composite to improve the electrical conductivity of inorganic materials. Thus, it is interesting to dedicate attention to other materials, for example, metal-organic frameworks (MOFs), pseudocapacitive materials, and layered materials that have a high potential to enhance electrochemical performance.
2. From the standpoint of electrolytes, it is expected that materials have high operating window, stability, low toxicity, and excellent ionic conductivity. The electrolyte has a key role in the storage mechanism. The kinetic balance between electrodes and electrolytes at interfaces needs to be better understood. The most common electrolytes employed are organic, aqueous, nonaqueous, ionic liquid, and solid-state electrolytes. However, each one possesses some drawbacks. For example, organic electrolytes are flammable and toxic. Aqueous electrolytes have a low working voltage range. Ionic liquids are expensive, not being suitable for large-scale commercial applications. Moreover, solid-state electrolytes, such as polymers, present poor interfacial resistance and low electrical conductivity. Thus, it is important to analyze each one in the set that makes to cell, considering the electrode materials employed to optimize the synergic effect of both electrode and electrolyte.
3. Other components, such as separators and current collectors, also have some importance in storage devices. The separators are responsible for separating the electrodes, avoiding electrical short circuits, and providing pathway for charge transport in the liquid electrolyte. Cellulose-based materials have demonstrated outstanding potential as an alternative to the common separators. On the other hand, current collectors support active materials such as cathodes and anodes and connect the electrodes in external circuit. The most common material used is carbon fibers, but these materials are expensive to be commercially used. Therefore, new materials need to be investigated soon. Up to now, few researchers have studied new materials as separators and collectors. Almost all focus on improving the electrode materials and electrolytes.
4. Another important point is the characterization techniques. Generally, CV, CD, and impedance are the common techniques used to evaluate electrochemical performance. However, it is necessary to comprehend the storage mechanism of SIHCs to improve the efficiency of the component materials. In situ nuclear

magnetic resonance spectroscopy, in situ infrared spectroscopy, in situ X-ray diffraction, and electrochemical quartz crystal microbalance are powerful techniques that can also be carried out.

The energy storage hybrid devices are still in development. The search for more efficient and low-cost devices is the main challenge for science because they directly impact large-scale commercial use. Driven by the electric vehicles market, the SIHC is a fertile field and still has great space for its development to be commercially available soon.

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