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Battery-Supercapacitor Hybrids: A Literature Review

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Abstract:

This literature review explains the construction and charge storage mechanisms in Lithium-ion batteries. Further, it elaborates on the electrode reactions in Lithium-ion batteries, and commonly used electrode materials and their structures. Different types of Lithium-based batteries' electrochemical performance were compared, in addition to other relevant differentiators. The energy storage mechanism in Supercapacitors is briefly touched upon – and the electrochemical performance of supercapacitors is compared with that of lithium-ion batteries. Battery supercapacitor hybrids are introduced, with a brief section on their development over the past two decades following explanations of the charge storage mechanism and construction of battery supercapacitor hybrids. Battery supercapacitor hybrids are then compared with existing electrochemical energy storage mechanisms and finally, two types of battery supercapacitor hybrids were discussed.

Keywords -Battery-supercapacitor Hybri, Comparative analysis, Lithium-ion battery, Supercapacitors

INTRODUCTION

Batteries are the primary means of energy storage in the contemporary, electricity-based world. With renewable sources of energy being the subject of intensive, global scale research, one problem presents itself above all others: where can we stock excess energy when the full combined capacity of power sources is not in use? Traditional means of energy



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generation involve burning fossil fuels to produce electricity, and when not needed he furnaces can function with minimal amounts of fuel as compared to their full production capacity. However, when renewable energy comes into play, we give up the ability to control the output power, with solar and wind farms depending on sunlight and wind speed respectively. This lack of control leads to the need for energy storage systems that fulfil a number of requirements: efficiency, energy density, power density, operating range and more importantly for large-scale applications such as powering entire cities cost per kWh of energy stored. Although the advent of new forms of energy storage, like gravity- based storage systems and heat-based systems are providing potential future alternatives, these technologies will likely remain concepts and prototypes for the next decade. Accordingly, we need a means of storing energy that can bedeveloped rapidly, whose concept has already been proven, and one that can be manufactured at a large scale using existing



technologies at a reasonable cost. Lithium based batteries are

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the first choice that comes to mind, however, the lower power density, and high cost inhibits continuous manufacturing. Moreover, their manufacture is unsustainable due to the relative rarity of naturally occurring lithium deposits. Supercapacitors (SCs) are the second means one deliberates, but the inherent high self-discharge rates combined with low energy density make them an unviable alternative for long term storage. However, in 2001, Amatucci et al¹. created a device that combines the energy density of a lithium-ion battery (LIB) and the power density of a supercapacitor - a Battery Supercapacitor Hybrid. These devices can provide a viable means to store energy, combing the best aspects of both LIBs and SCs in one device. Recent developments have allowed BSHs to be constructed from various types of batteries, namely Na-ion BSHs² as constructed by Kuratani et al..Although still in a relatively nascent stage of their development, BSHs have shown huge potential - and are the focus of this paper.

I. ENERGY STORAGE IN A GENERIC ALKALINE CELL

A battery creates a potential difference between its electrodes. It does this by creating a flow of electrons between the anode and cathode – through an external connection when a circuit is completed- which are separated by a fibrous barrier that allows only the flow of cations. On this separator is an electrolyte, and a core made of the cathode material. the zinc is in powder form to improve surface area thus reducing internal resistance. Both terminals are isolated from each other, generally by a nylon cap at the bottom end of the cell. This layout is shown in figure 1. The combination of the materials - manganese dioxide as the cathode and a gel which has zinc powder as the anode (in alkaline batteries) - causes a reaction. The zinc ion in the battery is oxidized and this releases electrons, which collect at the cathode. Simultaneously, the anode is reduced and with the repetition of these two reactions, there is an electron build up at the cathode which creates a potential difference across the terminals. When connected, the flow of electrons generates current and thus provides energy. When not in use, the battery stores energy chemically as described above.

II. ENERGY STORAGE IN A LITHIUM-ION BATTERY

A. Construction

A generic li-ion battery consists of an anode made of copper coated with graphite (recent technological advancements have led to the use of graphene). Its cathode is a lithium-based compound, normally LiCoO2 or LiFePO4. The anode and cathode are separated by an electrolyte, in which there is a dielectric separator. This layout is as shown in figure 2.

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C. Charge-Discharge

During charge, ions from the cathode pass through the electrolyte and are transferred into the lithium graphite anode,



layers are rolled into a cylindrical cell using the 'swiss roll method', as shown in figure 3. The layout is extremely thin and compact, the diagram above enlarging the width of the electrodes and electrolyte significantly. This layout is still in use today due to its hyper-optimized design.

For optimal packing efficiency into a cell, strips of thin



B. Why Lithiated metal oxides are used

Lithium-ion batteries are lightweight and have a high energy density, and they can be recharged rapidly. The element's high electrochemical potential makes it a valuable component of high energy-density rechargeable lithium-ion batteries⁶. Additionally, lithium is the least dense and lightest metal, which means more lithium atoms or ions can fit into the same volume than any other solid element. Further, of all elements, lithium has the least ionization energy due to its electronic configuration, so a minimal amount of energy is required to initiate the charge-dischargeprocedure. Lastly, lithium is highly reactive and this carries the implication that more energy can be stored in the bonds lithium forms than in any other element, which contributes to the high energy density of lithium batteries. To this end, lithiated metal oxides are ideal electrode material due to the fact that the most amount of energy and molecules can be squeezed into the same volume of space - maximising the electrochemical performance of a battery.

Figure 3 - Swiss Roll method of packaging a cell

they intercalate with the layers of graphite. The separator prevents them from flowing back into the cathode to a large extent, which reduces the self-discharge rate greatly. When current is required and the terminals are connected, ions intercalated with the graphite first release one or more electrons, and these flow through the means of connection and return to the cathode, where the cathodic ion has also travelled, through the separator, and once the compound is reformed, the battery is ready for charge. energy is stored in the lithiated metal oxide cathode in the form of the energy used to ionize that compound while charging –releasing the energy that caused ionization during discharge. This ionic movement can be visualized as in figure 4.

Figure 4 - A representation of ionic movement during charge and discharge

D. The Reactions that Occur in the Electrodes

1) At the Cathode⁷: During discharge, lithium ions migrate from the anode through the electrolyte medium to the cathode, where they are incorporated into lithium cobalt oxide through the following reaction, which reduces cobalt from a +4 to a +3 oxidation state. During charge, the reaction is reversed.

$$Li_{1-x}CoO_2(s) + x Li^+ + x e^- \rightarrow LiCoO_2(s)$$

2) At the anode': During discharge, lithium stays as Li+ in the lithium-graphite anode, while the carbon is reduced through the following reaction, which is reversed during charge

$$C_6Li \rightarrow 6C + Li^+ + e^-$$

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Figure 6 - (a) Spinel Structure of LiMn₂O₄; (b) lithium diffusion pathways

E. The Intercalation Mechanism:

LIBs operate by storing energy through the variable intercalation of ions in the electrodes. This is achieved through two means. Firstly, the anode material is graphite (In newer batteries, this is graphene and research is being carried out where silicon-based anodes are being experimented with). Graphite is a form of carbon composed of layers of tightly bound carbon atoms whose layers are loosely held together, as shown in figure 5^7 . It is between these layers that lithium ions are intercalated and where they remain until discharge.



Figure 7 - Li₄Ti₅O₁₂ Spinel Structure, Blue octahedra represent lithium, Green octahedra represent disordered lithium and titanium; red spheres represent oxygen

F. Commonly used Electrode Materials

Electrode	Material	Structure	Average Voltage (V vs. Li)	Practical Capacity (mAh/g)
	LiCoO2	Layered	~3.9	~140
Cathodes	LiMnO2	Spinel	~4.1	~120
	LiFePO4	Olivine	~3.45	~160
Amadaa	Graphite (LiC6)	Layered	~0.1	~360
Anoues	Li4Ti5O12	Spinel	~1.5	~175

TABLE 1 - COMMONLY USED CATHODE AND ANODE MATERIALS

G. Types of Electrode Structures

The following section will display the different types of structures as introduced in table 1.





2) Layered Structure^{11,12}:



*3) Olivine Structure*¹³:

H. Factors that affect Electrochemical Performance

as well as their micro-scale behaviours-



Figure 10 - Olivine Structure in LiFePO₄

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like ionic conductivity - affect the properties of the battery. These properties define the performance of the battery. The way a battery performs then goes on to alter its structure and chemistry – since a better performing battery will inevitably consume the reactive materials within it more rapidly than a lower performing one- resulting in a positive feedback loop of sorts. The factors that affect electrochemical performance of batteries are shown in figure 11^{14} .





Figure 11 - Factors affecting electrochemical performance

purple spheres represent lithium; peach represent cobalt

A. Electrostatic energy storage

Electrical energy is stored in supercapacitors via two storage principles, electrostatic double-layer capacitance and electrochemical pseudo-capacitance. Supercapacitors store less energy than batteries but release exponentially faster. They can also be charged faster than conventional batteries due to an inherent low energy density, and since energy is stored electrostatically, creating a charge difference at the terminals. When these terminals are connected, the oppositely charged particles quickly release from the plates they are ordered on and flow across extremely fast.

B. Asymmetric Supercapacitors

Asymmetric supercapacitors (ASCs) are assembled using two dissimilar electrode materials that offer the distinct advantage of a wide operational voltage window, which significantly enhances their energy density. Generally, metal oxides are employed as one of the supercapacitor electrodes, whereby RuO₂, MnO₂, and Ni(OH)₂ are the most commonly used materials¹⁵. Other materials can be used as the other electrode to fabricate ASCs, such as porous carbon. For example, ASCs employing aqueous electrolytes have potential windows of greater than 2.0 V. The energy density of ASCs can reach almost 100 W h kg-1. Based on these features, a higher ASC energy density can be obtained by utilizing organic or ionic-liquid electrolytes, which have higher working voltages¹⁵. Moreover, Misra et al.¹⁶ reported a tandem ASC with a high working potential of 4.5 V to provide a wider voltage window, which had an energy density that was 61% higher than that of single ASCs.

C. Pseudocapacitors

Pseudocapacitors store electrical energy both faradaically and non-faradaically by electron charge transfer between electrode and electrolyte. A pseudo capacitor has a chemical reaction at both electrodes, unlike EDLCs where the electrical charge storage is stored electrostatically with no interaction between the electrode and the ions. the capacitance of a pseudo capacitor may be higher by a factor of 100 as a double-layer capacitance with the same electrode surface.

IV. COMPARING ENERGY STORAGE SYSTEMS

A. Comparing Different Types of Batteries

In order to display the characteristics that batteries constructed with different electrode materials have, data was first assembled from a variety of sources, then tabulated in table 2. To provide a comparison for the benefits of the use of lithium, the same data was gathered for a Zn-air battery as well.



Figure 12 – Comparing Theoretical Specific energy densities of different batteries



As seen in table 2, LiS and Li-air batteries have a significant advantage over other types of batteries with respect to their theoretical specific energies - a measure of how much energy a battery contains in comparison to its weight. The best cycle lives- defined as the number of charge cycles a battery can be put through till it retains only 80% of its original capacity at a state of full charge, were exhibited by Li-ion batteries and Li-metal batteries. The cheapest type of lithiumbased battery is the LiS, and the cheapest overall was the Znair battery - costing 100\$ per kWh. Of all the batteries compared, LiPo and Li-ion batteries are the most efficient with energy efficiency defined as a measure of the energy that can be taken from the battery compared to the amount of energy that it was charged with beforehand. The specific energies and Figure 13 - Cycle Life of different Batteries cycles lives

are compared in figures 12 and 13 respectively.

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Battery type	Li-ion		Li-S	Li-air		Li-metal		LiPo	Zn-air
sub-type	LiCoO 2	LiFePO4	-	1 st cycle secondar y battery	2 nd cycle primary battery	Li-Co	Li-Cd	-	-
Theoretical Specific energy (Wh/kg)	387 ¹⁷	100 ¹⁸	2567 ¹⁷	3582 ¹⁹	11140 ¹⁹	150- 200 ²⁰	50- 60 ²⁰	500 ²¹	837 ²²
Typical cycle life	250-	1200 ²³	500 ¹⁹	>10	1	1000-	2000 ²⁰	350-600	120 ²²
cost/kWh	200-4	4000\$ ²⁴	200\$ ²⁵		-	40	0\$	600\$	<100\$ ²²
applications	Electric Portabl grid-sca storage	Vehicles, e devices, ale power e systems, etc	See technical maturity below	See technic bel	cal maturity ow	cordles pho emer ligh	s home nes, gency ting	Remote-controlled vehicles, consumer electronics	hearing aids, digital watches
energy efficiency	70%-	100% ²³	-		-	~88	3% ²⁶	>95% (between 20-40ºC) ²⁷	30-50% ²³
operating temperature range	10º0	C-80ºC	10ºC-60ºC		-	15ºC	-45ºC	5ºC-80ºC	10ºC-50ºC
Advantages	Very hig Very hig and di ra no mem Inhere Recy Low disch	th capacity low ESR gh charge ischarge ates nory effect ntly safer yclable v self- narge ²⁸	Low cost Non-toxic Very high energy density excellent performance at room temperature relatively lightweight (approx. 1000 kg/m^3)	extremely h ene lightweigh cath	nigh specific ergy t due to air node	low in resisi can sup surge c high cy	ternal tance ply high urrents rcle life	relatively low weight high power delivery high specific capacity	high energy density low cost Low active material utilization
Disadvantages	High Lowe vo h enviro impac usage sensitiv tempo unusa com discl	er cost er float Itage iigh inmental it due to of Cobalt ve to high eratures ble after nplete narge ²⁸	suffers from permanently reduced life and capacities under very high discharge rates, improper storage environments, from overcharging or from complete discharge. Moderate technical maturity Bad cycling stability	Still in earl develo Will be at years until availa Very low	y stages of pment least 5-10` commercial ability cyclability	Low s capa High Sm tempe range in effic	pecific acity cost nall erature n which cient	risk of fire if charged for a prolonged period tends to heat up under high load high cost	low power density Poor cycling stability of air cathodes
Technical Maturity	pro Commo	oven ercialized	Not commercialized More mature than Li- air, less mature than Li-	In developr Not com avai	ment phase mercially lable	mat comme	ture rcialized	mature commercialized	Mature commercialize d

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Energy Efficiency	70-100%
Self-Discharge Rate (% per day)	2-3

B. Comparing Li-ion Batteries with Ultracapacitors

In order to successfully show the advantages and disadvantages that Battery Supercapacitor Hybrids (BSHs) have as compared to both LIBs and Ultracapacitors (UCs), we must first compare LIBs and UCs by themselves. This comparison is carried out in table 3 and is represented visually in figures 14 and 15 – alternatives to each other with an aim to improve the ease of reading.

As can be seen, the specific energy and energy density of LIBs is significantly higher than that of UCs. However, when their power densities and specific powers are compared, UCs far outperform LIBs. Further, the cycle life of UCs is exponentially greater than that of LIBs - in part due to the absence of a reactive electrochemical storage mechanism. UCs, partly due to their intricate construction and developing progress, in addition to the inherent low energy density implying more UCs are needed for the same energy capacity, have a cost far greater than that of LIBs. However, UCs have little to no impact on the environment - with readily available carbon comprising the main raw material in their manufacture. LIBs on the other hand, require lithium and cobalt for their construction - elements that are scarce and expensive - and whose extraction causes significant environmental damage. Both LIBs and UCs are similarly efficient, with the potential to be completely efficient, although the electrostatic charge storage mechanism in UCs leads to a significantly higher selfdischarge rate.

	Li-Ion Battery ²³	Ultracapacitors ²³
Specific Energy (Wh/kg)	30-400	0.7-85.6
Specific Power (W/kg)	8-2000	5.44-100000
Energy Density (Kwh/m^3)	94-500	1-35
Power Density (KW/m^3)	56.8-800	15-4500
Cycle life (cycles)	250-1200	10000-1000000
Cost (US\$/kWh)	200-4000	300-20000
Environmental Impact	High	Very Low



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Figure 15 - Lithium-Ion Batteries vs. Ultracapacitors - Spider plot

V. BATTERY SUPERCAPACITOR HYBRIDS

A. Introduction

Despite their different electrochemical characteristics and behaviors, batteries and SCs share similar configurations, both include anode, cathode, electrolyte, separator, and current collector, making the hybridization feasible. The following sections will explain what BSHs are, their development over the years, and categorize them based on the materials used for their construction. further, they will describe the differences between BSHs and LIBs/SCs and evaluate the benefits of a hybrid device.

B. Construction

A BSH is an energy storage system that uses one battery electrode in conjunction with a supercapacitor electrode. A BSH contains one reactive, battery type electrode and one capacitive electrode which can be either EDLC-type or pseudocapacitive. Both the battery and SC electrodes can be used as either anode or cathode. Despite being asymmetric, a BSH is different from conventional "asymmetric SCs," in which both electrodes are capacitive but with asymmetric

Capacitive electrode Electrolyte Current Collector Current Collector

Separator

capacitive charge storage mechanism. BSHs typically, by virtue of their hybrid nature, can surpass the energy density of conventional asymmetric SCs and could potentially outperform batteries with respect to their inherent power density limitations due to the combination of a capacitive electrode and the technologically mature battery electrode to warrant faster electrochemical kinetics. Further, the total theoretical capacitance of the capacitive electrode could be employed for practical applications and the range of possible output voltages could be widened through selecting an ideal battery-type electrode that can operate in a separated potential range. A diagrammatic representation of their construction is shown in figure 16.

C. Charge-Discharge mechanism in BSHs

During charge and discharge, ions move between the two electrodes and the bulk of the redox reactions occur on the battery-type, reactive electrode. Ion accumulation and separation, which allow rapid charge transfer and thus the superior power densities that BSHs have, occur on the capacitive electrode. Simultaneously, there is an electron flow occurring on the external circuit connection which is the source of useful energy.

Figure 16 - Representative Construction of a Generic BSH

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1) Charge :When a BSH is charged, several processes occur simultaneously. The following section will elaborate further. Figure 17^{29} displays differences in charge and discharge mechanisms of several different energy storage systems

2) Charging the Capacitive electrode: As current is passed through the battery, the electrolyte is ionized, and the anions formed from its dissociation are attracted to the capacitive electrode. Upon reaching the anode, they are ordered on the activated carbon, which, due to its porosity, has an extremely large surface area on which these ions can order themselves. This creates a negative charge on the anode and a positive charge in the electrolyte – which is then composed of cations.

3) Charging the reactive electrode: This electrode functions similarly to that in a battery, where Li+ ions are intercalated into a graphite/graphene electrode, but from the electrolyte instead of an oppositely charged electrode containing the Lithiated metal compound

4) Discharge: When the two terminals are connected, the capacitive electrode releases its electrostatically charged energy in conjunction with the reactive electrode. The energy is released at a high rate for a generally longer period than in a battery, due to the asymmetrical construction. By virtue of the electrostatic storage of charge in the capacitive electrode, it wants to release the charge as quickly as possible, but this release is restricted in ways by the relatively slower energyrelease mechanism in the reactive electrode – and a middle ground of discharge is reached

Figure 17 - diagrammatic representations of charge-discharge (a) in ELDC; (b) LIB; (c) Pseudocapacitor; (d) BSH

D. Progress in BSHs since their invention

One of the earliest hybrid SCs is the Li-ion based BSH, which was named, reported, and patented by Amatucci et al¹. in 2001. Li-ion BSH was assembled with a nanostructured $Li_4Ti_5O_{12}$ anode and an activated carbon cathode. With the high specific capacity of Li-ion type electrode, Li-ion BSHs bridged the gap between LIBs and SCs and attracted worldwide attention.

Li-ion BSHs were developed with the goal to have energy densities compared with supercapacitors while at the same



Figure 18 – Ragone Plots of various rechargeable batteries and ELDC, and the comparison with BSH $\,$

time retaining the power and most importantly the notorious cycle life and robustness of a supercapacitor. To increase the energy density of the supercapacitor by a factor of 5-10 and maintain cycle robustness, a non-aqueous asymmetric hybrid configuration was developed incorporating a capacitive or pseudocapacitive positive electrode coupled with a Li-ion insertion. The most challenging properties to overcome was the ability to maintain >100,000 cycles and the ability to accept full charge within 15 seconds³⁰. For example, a composite/nanocomposite of LiCoO₂ and activated carbon can be fabricated and applied as the positive electrode. The ratio of intercalation material and activated carbon further expanded the flexibility of the energy storage cell to be tuned to a specific device's requirement. The composite packaged cell exhibited 20- 35Wh/kg at 2000-3000W/kg as an experimental prototype in 2004, and was able to withstand over 3000 cycles³⁰ even with an output as considerable as that mentioned above. The ragone plot below (figure 18) shows the current and future potential for BSHs.

E. Comparing BSHs with Conventional energy storage mechanisms

This section will compare the electrochemical performance of BSHs, both those that currently exist and those whose prototypes are in the making, with the electrochemical performance of LIBs and UCs. By doing this, one can fully grasp the potential that BSHs hold and why they could be the ideal power storage mechanism when completely developed. This comparison is carried out in table 4, with diagrammatic representations through figures 19 and 20.



performan	ce d fi-lldB s, U Batteries ²³	JCs BSHs Ultracapacitors ²³	BSHs – current generation ³¹	BSHs – future generation ³¹
Specific Energy (Wh/kg)	30-400	0.7-85.6	25-200	50-500
Specific Power (W/kg)	8-2000	5.44-100000	400-5000	1000-20000
Cycle life (cycles)	250-1200	10000+	10000+	10000+

TABLE 4 - COMPARING THE ELECTROCHEMICAL PERFORMANCE OF BSHS WITH LIBS AND UCS





F. Types of Battery-Supercapacitor Hybrids

1) Li-ion Batteries: With almost the lowest lithium intercalation potential and highest cycling stability among all

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viable Li-ion anodes, prelithiated carbon materials such as graphite are one of the most suitable anodes for organic Li-ion BSHs. Li-ion BSHs assembled using battery-type lithium-intercalation cathode and capacitive carbon anode are also advantageous and generally have high working potentials, due to the high-voltage plateau of the cathode.¹⁵

Anode materials such as Ti-based oxides, silicon³², Fe3 $O4^{33}$, and intercalated carbon, and cathode materials of spinelLiMn₂O₄³⁴ Li₂CoPO₄F³⁵ and their hybrids with various conducting carbon/polymers were investigated for Li-ion BSHs³¹

Zhang et al.³⁶ applied commercial activated carbon as the cathode and mesocarbon microbeads as the anode, achieving a maximum power density of 5500W/kg and energy density of 92.3 Wh/kg.

Nanostructured hybrid electrodes represent a promising avenue to obtain advanced energy storage devices with excellent performance. With this, enhanced electrochemical properties such as fast charge transfer kinetics and ultralong cycling stability were realized.³¹ Further, Metal oxide nanostructures are promising electrode materials for lithiumion batteries and supercapacitors because of their high specific capacity/capacitance, typically 2–3 times higher than that of the carbon/graphite-based materials.

For example, hybridized nanostructured electrodes of battery-type materials with advanced carbon were demonstrated the most effective to achieve ultrafast charging and discharging. Li4 Ti5 O12 -based Li-ion BSH is the most widely studied hybrid device since the Ti-based anodes can completely avoid the electrolyte decomposition¹

Naoi et al.³⁷ utilized "ultracentrifuging treatment" to attain "nano-Li4 Ti5 O12 /carbon" anode. This nanoelectrode even showed a high capacity of 78 mAh/g at 1200 C rate (3 s charge–discharge) and the full cell could reach an energy density of 28 Wh/L at 10 kW/L, which shed light on how to design high-performance battery-type electrodes for BSHs. A similar concept was also demonstrated for Nb₂O₅ anodes^{38,39}; with the design of mesoporous or core–shell structured Nb2 O5 /carbon anodes, the BSH devices exhibited very high power densities, at which high energy densities were still maintained (eg: 16Wh/kg at 18kW/kg)

Although the specific capacity of intercalation cathode is lower than most of the battery anodes, it still has much higher charge storage ability as compared to the capacitive cathodes in EDLC device and shows great promise to boost the energy density of the BSHs³¹.

Brandt et al⁴⁰. reported a high-power Li-ion BSH based on LiNi0.5 Mn1.5 O 4 and activated carbon; with the cell voltage of 0–3.3 V, this device showed capacity retention of 89% after 4000 cycles, maintaining average specific energy

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density and power density of ~50Wh/kg and ~1100 W/kg respectively

Aqueous Li-ion BSHs is another attractive hybrid device due to the high safety (non-volatile, non-flammable, and nontoxicity) and high ionic conductivity of aqueous electrolytes as well as the simplified device assembly process³¹.

2) Na-ion BSH: LIBs have had a monopoly on the electrochemical energy storage sector for portable devices since the 1990s. although they have their benefits, the lithium supply is severely limited, and its extraction is an expensive process. Sodium, however, is present in abundance and due to similar chemical properties to lithium, it provides a viable alternative to Li-ion batteries. Sodium-ion based storage systems are not in their embryonic stage technologically, with the earliest sodium intercalation material (TiS₂) reported in 1980⁴¹. More recently, O₃ layered metal oxide cathodes were demonstrated as potential electrode materials for Na-ion batteries.

Combining the merits of both Li-ion BSHS, and Na-ion batteries, Na-ion BSHs have been the subject of intensive development over the past decade. The configuration of the device can be similar to that of Li-ion BSHs with either organic or aqueous electrolytes. Accordingly, carbon//carbon matching - a non-expensive way to coat carbon on the Nametal oxide electrodes. This has been widely investigated in the development of NA-ion BSHs. Carbon coatings on the electrodes have the potential to double their cycle life 43 – with Superior cyclic stability of the carbon coated product with capacity retention of more than 80% after 1000 cycles of charging/discharging demonstrated with an optimum carbon thickness matching commercial samples.⁴³However, due to the relatively low capacity of hard carbon in Na-ion electrolyte, the electrochemical performance of the device is inferior to that obtained in Li-ion electrolyte. To improve the device's performance, the delicate design of micro-/nanostructures of electrodes is very important. In general, fast Na intercalation kinetics and high surface area should be ensured for the reactive carbon anode and capacitive carbon cathode, respectively.³¹

very low potential hysteresis between charge and discharge processes was attained for anode and ideal EDLC behavior of the cathode was achieved by Ding et al.⁴⁴ in 2015. The group assembled a carbon//carbon Na-ion BSH, with both electrodes derived from peanut shells, resulting in highly flaky, thin, and porous carbon materials. The anode carbon was designed with partially ordered thin graphene domains while cathode carbon was with large surface area and high levels of oxygen doping, providing fast Na + diffusion and abundant redox active sites as well as massive ion accumulation and pseudocapacitive reaction. Consequently,

this Na-ion BSH exhibited excellent power and energy densities (201, 76, and 50 Wh kg -1at 285, 6500, and 16 500 W kg-1, respectively).⁴⁴

VI. CONCLUSION

This literature review has elaborated on the workings of BSHs and LIBs and UCs. Diagrams and illustrations were used to simplify concepts introduced and explained throughout this paper. A tabular format was used where possible to assist the comprehension of the data presented with visual representations present for the same purpose. Lithium-ion batteries, while a good means of energy storage will be outperformed by Lithium-Sulfur and Lithium-air batteries when they have been developed fully - due to them being more cost-effective, the raw materials being more abundant and most importantly because of better performance. electrochemical However. Batterysupercapacitors hybrids can be derived from these Li-based batteries as well, opening avenues for research on BSHs. BSHs are high performing energy storage systems, but they do no match the specific power of ultracapacitors - leading me to believe that for applications that require high specific power systems, a bank of UCs should be used- at least until BSHs are developed sufficiently to compete with UCs.

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