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To What Extent Can Organic-based Sodium-ion Batteries Replace Technologies Employed in Modern Day Secondary batteries?

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Abstract

The rapid growth of lithium-ion batteries sparked a drastic increase in the amount of lithium extracted from mining sites, which consequently leads to problems such as unsafe working conditions, child labour, and resource depletion. Since organic-based hybrid batteries and sodium-ion batteries are becoming increasingly prevalent, these technologies are compared with current technologies such as lithium-ion batteries in terms of electrochemical performance, sustainability, and economic viability. The data used in this dissertation is mostly acquired from academic journals and government websites, and source validation is used to evaluate the trustworthiness of each information outlet. By the end, an analysis of the feasibility of the organic batteries are compared against lithium-ion batteries, and further research is proposed to heighten the possibilities to incorporate sustainable materials into uprising batteries.

Keywords: energy density, power density, overvoltage tolerance, self-discharge, cycle life, current density, organic electrodes, lithium-ion batteries, sodium-ion batteries

1. Introduction

As the modern world shifts towards digital technology, human's dependence on electrical devices has accelerated over the recent decades. According to Internet World Stats, the percentage of the world population that has access to the internet increased from 0.4 to 69.0 % from 1995 to 2022, which is evident for how quickly the digital revolution has consumed our society. Recently, there has also been a rapid increase in electric vehicle's popularity. In the overall car market, the market share of electric cars has risen from 4% in 2020 to 14% in 2022, and is projected to increase further to 18% by the end of 2023. What is common to the aforementioned electrical machines are batteries, specifically lithium-ion batteries, which is a widely accepted technology that is projected to grow by over 30% annually from 2022 to 2023, according to McKinsey & Company. Lithium-ion batteries yield unrivalled electrical properties as lithium contains the least reduction potential in all elements. They are also the third lightest element on the periodic table and they have the smallest ionic radii, allowing the battery to have high capacities, energy density, and power density[1].

Despite these attractive electrochemical properties, lithium ion batteries poses significant social and environmental issue that is often overlooked, including child labour, toxic waste disposal, and strenuous

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consumption of transition-metal resources[2], which will further be expounded in section 2.

Fortunately, a recent focus on organic-based hybrid secondary batteries attracted numerous researchers to explore its potential to replace lithium-ion batteries. In short, organic batteries are environmentally friendly and functionalizable alternatives to current cathodic materials which employ high amounts of transition metals such as cobalt. Unlike full organic battery where both the cathode and the anodes are made up of organic materials, hybrid organic batteries contain one electrode that are made up of organic materials, and is selected for this research because full organic batteries suffers from the dissolution of organic electrodes into organic electrolytes which caused poor cycling capacity and rate capabilities[3].

Previous research has shown that organic batteries are becoming increasingly applicable in metal-ion batteries. These are mostly done through presenting their electrochemical results from analysis methods such as charge-discharge curves, cycling stability, and cyclic voltammetry[4] [5] [6] [7] [8]. However, to my knowledge, only a few research papers have created significant discussions on the potential replacement of lithium-ion batteries by organic-based hybrid batteries. Hence, this dissertation aims to evaluate, in detail, the extent to which prospective organic-based batteries can replace conventional LIBs.

I have analysed the conventional batteries of the present including lead-acid, nickel-cadmium, nickel-metal-hydroxide, and lithium ion batteries, and assess the prospective hybrid organic-based sodium ion batteries including activated carbon from rice husks, poly(9,10-phenanthraquinone-alt-benzene), and $MoSe_2$/graphene nanocomposite metal-organic framework. These technologies are then objectively evaluated and selected for the final comparison in terms of electrochemical performance, sustainability, and economic viability. The discussion and conclusion is then made regarding the potential replacement of lithium-ion batteries from hybrid organic batteries to evaluate the extent at which organic-based batteries can replace conventional batteries.

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2. Literature Review

Introduction to carbon

Carbon is a group 4 element in the periodic table, found in almost everything people see today from wooden tables to bouquets. It is also one of the most abundant elements in the observable universe and commonly found both aboveground and in subsurface regions of the earth's crust. In this dissertation, carbon is one of the most prevalent elements that contributes to Section 2 of the literature review.

Introduction to organic compounds

Generally speaking, organic compounds are chemical substances that contain carbon(s) as its main constituent framework. Nearly all living matters in the universe are dependent on organic compounds to survive. Humans are no exception. For instance, we consume protein, fats, and carbohydrates to derive energy[9]. And there are several types of existing organic compounds that will be presented in this literature review. The main carbon structure is often referred to as the 'carbon chain'. When several atoms of different elements chemically bond to the chain, it forms functional groups such as alcohol, quinones, carbonyls etc. which categorises organic compounds into families called "homologous series".

Due to its abundance and sustainable production processes[10], several industries that were once dependent on inorganic earth resources are now shifting their focus towards organic compounds as modern society places significant emphasis on sustainable development and resource conservation. A vivid example of such transformation is already visible in the battery industry where numerous researchers have incorporated organic compounds into metal-ion based batteries to reduce the heavy exploitation of metal minerals in the earth's crust.

What are batteries and how do they function?

A battery is an electrochemical device that converts stored chemical energy into electrical energy. Generally, batteries are composed of four main components: the electrodes (anode and cathode), the separator, and the electrolyte. The anode is an oxidation site where atoms lose electrons to form positively charged ions and release electrons into the external circuit. The cathode, on the other hand, provides a reduction site for positively charged ions to be reduced back into atoms as it uses the electrons from the external circuit. As electrons accumulate at the cathode, the positive metal ions are attracted towards it, and the electrolyte serves as a medium for ion movement between the electrodes. The separator is made up of permeable polymeric membranes which allows ions to pass but not electrons. Hence, the movement of electrons in the external circuit creates a flow of charge, which is the current[11].

What makes an effective battery?

An effective battery typically contains high energy density despite its miniature dimensions, high power density/discharge rate, extended charge-discharge cycle performance, is safe to use, is extremely lightweight, is cheap and is environmentally friendly. But frontline technologies of the modern day world are deprived of this ideal battery — most batteries today put up stellar performances in a couple of ways but are also lacking in other parameters. For instance, Lithium-ion batteries contain advantageous properties such as long life cycle, high energy density, and high power density which intertwines to create a large discharge rate but they are

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sourced from Li, Co, Mn and other rare earth metals which releases toxic chemicals into the environment. The revolutionary battery of the future is bound to be one that excels in all these parameters, and this dissertation aims to constantly refer back to these factors. Therefore, organic-based batteries are fully evaluated on its potential to replace lithium ion batteries.

The Current Technologies

Table.1

Specification	Lead-acid	Nickel-cadmium	Nickel-metal-hydroxide	Lithium-ion
Energy density	30-5	45-80	60-120	110-160
Power density	180	150	250-1000	1800
Nominal Voltage	2V	1.25V	1.25V	3.6V
Overvoltage tolerance	High	Moderate	Low	Very Low
Self-discharge	Low	Moderate	High	Very low
Operating Temperature	-20-60°C	-40-60 °C	-20 - 60 °C	-20-60 °C
Cycle life	200-300	1500	300-500	500-1000

[12]

Current technologies analysis

Power output:

With LIBs' 1800 W/kg power density as shown on Table 1, drastically greater than any other types of modern batteries, their batteries are able to output the greatest amount of electrical current per unit time. Due to the positive correlation between power density and cell voltage, LIBs have the greater potential to "push" electrons, generating greater currents than other batteries. This relationship is supported by the nominal voltage value as LIBs hold the highest nominal voltage. Hence, LIBs has the most potential for heavy-current requirement applications, allowing it to become more versatile and scalable to many industries.

Safety:

In terms of user-protection, LIBs suffer significantly. As shown on the table, the overvoltage tolerance of LIBs is extremely diminished in comparison to other types of batteries, with Lead-acid batteries at the top. Lead-acid batteries, therefore, can endure longer periods of extreme voltages (exceeding its rated voltage) with reduced risks of thermal runaways. Hence, lead-acid batteries are the safest to use and LIBs are bound to the most risk of accidents, which have occurred in many instances during recent years.

Durability & Battery life

LIBs contain the least self-discharge rate compared to other batteries listed in the table, suggesting that it loses the least chemical energy over time when stored without use. This means that LIBs have to be charged less frequently and contain a longer battery life. It also contains a relatively high cycle life of 500-1000 cycles, only losing out to the Ni-Cd batteries with an average

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of 1500 cycles. However, Ni-Cd operates at a higher temperature than all of the batteries. Conclusively, Ni-Cd Batteries maintain their overall capacity for a longer period of time but lose battery without use at a greater rate and operate at a higher temperature in comparison to LIBs.

In this dissertation, we need the strongest battery to compare with the rising technologies in Section 3. Hence, we will use a scoring system to objectively determine the optimal battery. The score will be based on performances shown on Table.1 and each battery type will be rated on a score of 1 to 4. Any tie will be given the same score on the higher level.

Table.2

	Lead Acid	Ni-Cd	Ni-MH	Li-ion
Energy density	1	2	3	4
Power density	2	1	3	4
Nominal voltage	3	2	2	4
Overvoltage tolerance	4	3	2	1
Self-discharge	1	2	3	4
Operating temperature	4	3	4	4
Cycle life	1	4	2	3
Total score	16	17	19	24

Overall, LIBs scored the most overall points based on battery performance and real-world feasibility which is why it will be compared to *The Rising Technologies.*

Lithium-ion batteries

Lithium-ion batteries consist of Lithium ions which are intercalated within the graphite layers of the anode, a cobalt oxide cathode, and, typically, a lithium hexafluorophosphate solution as the electrolyte which acts as a medium for lithium ion transport. The Li atoms get oxidised at the anode and lose electrons when they are connected to an external circuit to form positively charged Lithium ions. The free electrons flow from the anode to the cathode (from negative to positive) since the collective oxidation of Li at the anode creates a region of high electron density which induces large negative charge. In conventional Lithium Cobalt Oxide batteries used in commercial applications, Cobalt plays a major role in receiving electrons at the cathode. As the density of electrons in cobalt increases, the Li^+ moves through the permeable polymeric membrane to intercalate between the Cobalt Oxide layers. This gradual transfer of Li^+ to the cathode balances the increasing negative charge from electrons at the cathode and allows a continuous flow of electrons. Therefore, current is produced to power the electrical appliances.

In terms of electrochemical performance, lithium-ion batteries shows a high average specific capacity of 850 $mAhg^{-1}$ average specific capacity when applied with a 500 mAg^{-1} current density, which coincides with a high energy density of 300 $Whkg^{-1}$ and power density so electrical devices will receive high current flow[13]. The theoretical specific capacity of LIBs can reach up to 274 $mAhg^{-1}$, and the capacity retention rate of this value is 96% in over 50 cycles[14]. This high energy

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density allows LCO batteries to produce a working voltage of 3.6V. The coulombic efficiency of Lithium cobalt oxide is 92.3%[15].

The market size for lithium-ion batteries, especially Lithium-Cobalt-Oxide batteries are expected to expand from $30B in 2017 to $100B in 2025 due to its widespread use in electric vehicles, mobile phones and laptops. However, LIBs pose great challenges for the planet and for the people involved. The main contributor to the unsustainable practices of LIBs root from the used ones. From the year 2000 onwards, 500 million cells have been produced worldwide. 200-500 million tonnes of waste created by LIBs are produced annually[16]. Most of them are left to accumulate in landfills because most lithium metals are lost as slag and its recycling requires the high associated energy[17], encouraging people to use the landfill as a cheap, yet effective alternative. Due to the flammable electrolyte and polymeric membrane, and toxic substances that comprise each electrode (cobalt), the disposal of Lithium ion batteries severely affects the balance of landfill soils and human communities alike[18]. Furthermore, the extraction of cobalt used in the electrodes of LIBs creates several adversities. 70% of cobalt is sourced from the Democratic Republic of the Congo (DRC), where 90% of it is derived from industrial mines[19]. However, in a developing country like the DRC, mines throughout the country have attracted thousands of workers, causing child labour in unsafe working conditions.

These downsides of lithium-ion production and usage are the key issues that this dissertation aims to tackle, whereby newfound and disruptive technologies are ones that will be able to overcome the prevalence of lithium-ion batteries. Recycling LIBs is a challenge, rooting from varying mixtures of chemicals and high embodied energy[20] which makes such efforts less feasible economically and environmentally[21].

On the other hand, researchers have recently shifted their focus towards the integration of sustainable organic compounds in batteries' electrodes[22], which will be further exemplified in the following section.

The Rising Technologies

This section of the literature review explores several prospects of organic-based batteries with the potential to develop or even replace current Lithium-ion batteries on an industrial scale. Three divergent organic containing batteries will be discussed, two of which will be the integration of organic compounds into the electrodes to enhance Lithium ion batteries, and the third will provide information on a full organic battery. Each organic technology will be evaluated in the same way as the previous analysis of non-organic batteries to ensure objectivity. However, sodium-ion batteries (SIBs) will be considered instead of LIBs since sodium is the sixth most abundant element on earth, which comprises 2.6% of the Earth's crust. Similar to lithium, sodium is an alkali metal with similar chemical properties and intercalation kinetics, yet are cheaper for

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industrial production and more sustainable. Also, sodium can be extracted from sea water, reducing the adverse effects of mining. Ultimately, this dissertation presents a more sustainable alternative to lithium ion batteries by showing different organic materials which can be incorporated into sodium ion batteries.

What are organic batteries

Hybrid organic secondary batteries are energy conversion systems that integrate organic compounds into the battery[23] [24]. These not only include the use of polymer-based electrochemically-active materials in the electrodes but also auxiliary components such as separators, electrolytes and additives[25]. In batteries, organic compounds that contain electroactive functional groups can carry out electrochemical reactions which electron flow[26].

The advantages and disadvantages of using organic batteries

With increasing attention for environmental concerns, organic structures have brought in extensive research in this field. Firstly, organic compounds are one of the most abundant families of substances on the planet because all living organisms rely on these substances for their survival, as stated in section 1. This further brings advantages such as low-toxicity which mitigates the disposal problems to the environment, preserving the biodiversity of wildlife while reducing exploitation of rare earth metals such as cobalt and substances in relatively low abundance such as lithium[27]. And for the same reason, this rich availability of organic compounds leads to lower cost to source and transport raw materials[28]. Additionally, organic electrodes are extremely sustainable because they can be recycled at various stages of charge due to their minute molecular size[29]. This reduces resource consumption on what is already abundant in the long run. Furthermore, since organic batteries can be made from any electrochemically active reagent, there is high structural diversity to tailor the batteries to differing applications.

Hybrid batteries Analysis

Metal-organic-framework/Graphene Derived Hybrids in sodium ion batteries

First discovered in 2004, graphene is a monolayer carbon plane in a honeycomb structure covalently bonded in the layer by strong covalent bonds. Graphene is electrically conductive, lightweight, durable, and forms high charge carrying capacity batteries that can last for a long time but only requires a quick charge. Its outstanding electrical conductivity results from its bonding: each carbon atom can form a maximum of 4 bonds, but graphene only contains 3 bonds, forming a delocalised pi electron that can move around freely to carry charges.

The diffusion time constant for ions to travel from one electrode to another can be defined by ($t \approx L2/D$), where t is the time constant, L is the transport distance and D is the diffusion constant. Since graphene is a

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monolayer material, it possesses extremely low diffusion distances, allowing for heightened power density of a battery[30].

Graphene, however, tends to stack up at the anode into graphite again, which is financially and electrochemically undesirable. But graphene itself can act as a conductive substrate that anchors other redox-active nanoparticles, mitigating aggregation of these particles during lithium ion transfer that can lead to severe electrode fracture[31] [32]. The nanoparticles, however, provide significant benefits for graphene as it reduces restacking which maintains the large surface area for electrochemical reactions. And to reduce the demands for lithium overall, graphene-based nanocomposite electrodes SIBs have been chosen for this dissertation.

SIBs work in a similar fashion to LIBs, with the only difference being the change from lithium ions to sodium ions as the mobile ion. The electrochemical performance of SIBs, in this case, are enhanced by depositing $MoSe_2$ nanosheets onto the surface of reduced graphene oxide (rGO), whereby the two heterogeneous layers forms interfacial attraction through C-O-Mo and C-Mo. This not only allows increased volume fluctuations for sodium ions with large atomic radius but also maintains a high rate of electron transport between each layer. Consequently, the discharge-charge specific capacity of the $MoSe_2$@5%rGO was shown to be 712.7-458.3 $mAhg^{-1}$ with the coulombic efficiency of 64.3%. The sample displayed high capacity retention of 383.6 $mAhg^{-1}$ after 50 cycles and produced outstanding reversible capacity of 435.3 $mAhg^{-1}$. These results displayed that rGO-$MoSe_2$ heterogeneous nanocomposites contain high cycling stability[33], high energy density of 196.9 $Whkg^{-1}$, and extremely high output power and high power capabilities[34].

Despite its high electrochemical properties, graphene is currently limited due to a number of reasons. The predominant limitation of graphene in the modern world is the lack of mass production method because it is hard to produce large sheets for commercialisation. One of the most common ways to produce graphenes is by mechanical exfoliation - using sonication methods or even pressurised CO_2 to intercalate between the graphite layers - which takes tremendous amount of time to isolate and only produces small amounts of graphene, preventing graphene to be used in the battery market. And because of this, the production of graphene can cost thousands of dollars per kilogram, which is tremendously higher than other carbon allotropes such as graphite and activated carbon[35].

Physically activated carbon from rice husks as electrodes in sodium ion batteries

Activated carbon is an amorphous allotrope of carbon derived from any biomass which has been treated/doped either by physical or chemical methods to increase the specific surface area[36]. Conventionally, a biomass is calcined under reduction conditions at approximately 1300-1500 °C[37], then mixed with

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chemical activators such as potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), or phosphoric acid (H_3PO_4) etc. These chemical substances attack and decompose the lignocellulose structure within the plant-based structures while increasing the pore volumes inside the carbon samples. The slurry between chemical activator and the carbonised biomass is then pyrolysed at a range of 800 - 1000 °C to both further break down the biomass structure and provide an optimal operating temperature for chemical activators. These activated carbon are then formed into a slurry with polymeric binders and inserted into the electrodes of batteries to act as electrochemical sites[38].

As there is a lot of bio-waste from sources such as agricultural sites and food industries, activated carbon acts as a twin-pronged solution to both waste management issues and sustainable batteries production. In other words, we are converting bio wastes into a higher-value product that can be commercialised[39].

It is, however, difficult to settle on a precursor of activated carbon that can be compared with other types of batteries. Therefore, the chosen precursor for the synthesis of activated carbon is rice husk because they are abundant across the globe as an agricultural by-product, with approximately 1.5E+8 tonnes produced annually[40] [41] [42] [43] [44] [45]. With the high content of lignocellulosic structure (including lignin, cellulose, and hemicellulose), rice husks have the ability to form great volumes of pore areas, which leads to increased surface area for electrochemical reactions[46].

From electrochemical analysis, the batteries using activated carbon as the electrodes show a high average specific capacity of 265 $mAhg^{-1}$ and 166 $mAhg^{-1}$ after a current density of 500 and 1000 mAg^{-1} has been applied, respectively. These samples also displayed a large specific capacity of 346 mAh after 100 cycles which, calculated, results in a 85% capacity retention. Furthermore, these batteries contain an energy density of 185 $Whkg^{-1}$ with an average output of 3.4 V. These results show that, relative to other SIBs, activated carbon is a promising material for electrodes production. Further details and comparison will be included in the discussion section.

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However, there are disadvantages that reduce the feasibility of activated carbon being widely commercialised. One of the main problems is that the synthesis of high porosity activated carbon from lignocellulosic biomasses requires immensely high temperatures throughout the process. Some precursors of the carbon requires 2 heat treatment stages including either hydrothermal carbonisation (at 180 °C for 24 h[47]) and pyrolysis (at 600 - 700 °C[48]) , or calcination (at 600 - 800 °C[49])) and pyrolysis to allow heat to decompose the lignocellulosic structure[50] [51]. When applied on an industrial scale, these strenuous heating cycles increased the demands for fossil fuel combustion to produce thermal energy used to heat this. Another issue regarding the synthesis of activated carbon is that most precursors are derived from waste biomasses, which fluctuates in supply during each season. Hence, industries may not prefer an unreliable source of raw materials.

<u>Poly(9,10-phenanthraquinone-alt-benzene) (PPQ) cathodes in Na-ion batteries</u>

Quinones are a family of organic compounds containing six carbon atoms arranged in an unsaturated ring (containing double bonds) with two carbonyl functional groups attached to it. Because of the availability of pi-electrons in the double bond, these quinones can conduct electricity, making them redox-active molecules with high electrochemical reactivity.

Additionally, the hexagonal aromatic rings of quinone contain delocalised pi electrons which are free to move around and carry charges, giving quinones the property to conduct electricity and form redox-active cathodes. Specifically, these 9,10-phenanthraquinone (PQ) are extremely suitable as monomers for PPQs because their skeletons contain two high pi electron density in conjugated phenyl groups. Their structure, therefore, contains higher delocalised electron density in the polymer which leads to increased electrical conductivity.

What's preventing the advancement of organic electrodes is that there are very limited capabilities for industrial-scale applications since numerous types of working organic electrodes dissolve into the electrolyte which results in a low cycling stability. However, PPQ is insoluble in aqueous and largely insoluble in other organic solvents due to its large molecular size and strong London dispersion forces between its molecules which strongly binds them together. Phenanthraquinone is an organic compound composed of two aromatic rings connected to two carbonyl groups to form a planar aromatic structure. And because of this, PPQ-based cathodes produced satisfactory cycling performance over extended periods of use.

Electrochemical analysis of PPQ demonstrated great results for future applications. Half-cell evaluations of cathode performance of PPQ presents the insoluble electrodes to show a moderate specific capacity of 104 and and 70 $mAhg^{-1}$ when applied a current density of 500 and 100 mAg^{-1}, respectively. Also, these samples show a high specific capacity of 150 mAg^{-1} over 300 cycles, which is retained over 300 cycles with insignificant attenuations. After 700 cycles, the discharge capacity decreases from 90 to 84 $mAhg^{-1}$ which corresponds to 93.3% capacity retention. Moreover, the average output of the half cells shows a moderately high voltage of 2.2 V.

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In terms of scalability, PPQ electrodes can be applied on an industrial scale because all the reagents used in this experiment are already commercially available and do not require any further purification. Phenanthraquinones, however, pose challenges for the environment, the battery industry and the people. For one, quinones are aromatic compounds derived from benzene and naphthalene[52], compounds that can be found in fossil fuels and crude oil. Therefore, even though we are pushing to create sustainable battery production, the main raw materials of quinone batteries source from a non-renewable resource. Also, PPQs and other aromatic compounds such as benzenes are mutagens so they are highly carcinogenic for workers in these industries[53]. Not only that, the synthesis of PPQs themselves require sophisticated procedures, including Friedel-Crafts reactions using isopropyl-substituted benzenes with phthalic anhydrides, then cyclisation of the products using sulfuric acid. These results in a mixture of anthraquinones which are then required to be purified further[54]. These complicated processes can result in bottlenecks and slow manufacturing processes.

Comparing organic-based sodium-ion hybrid batteries:

In this dissertation, we need the highest performing organic-based sodium ion battery to compare with the current lithium-ion battery selected in section 2. Hence, we will use a scoring system to objectively determine the optimal battery, similar to table.2. The score will be based on performances on Table.4 in every quantitative data shown and each battery type will be rated on a score of 1 to 3. Any tie will be given the same score on the higher level. Table.3 shows a summary table on the data used to objectively determine the organic battery for comparison. The energy density of the PPQs electrodes cannot be determined since there is an extremely limited amount of research done on the applications of phenanthraquinone's applications on batteries. Hence, PPQs will be given an average score of 2.

From table.3, the score of MOFs/Graphene and activated carbon are tied at 9. But because they excel in different aspects for a battery — that is, MOFs/Graphene for electrochemical performance and activated carbon for sustainability — both types of organic batteries will be evaluated against LIBs in the discussion section.

Table.3

	PPQs	Activated carbon	MOFs/Graphene
Average specific $mAhg^{-1}$ capacity after applied a current density of 500 mAg^{-1}	104	265	402
Cycling stability	No signs of attenuation from 150 mAhg-1 after 300 cycles	93% capacity retention after 100 cycles	95.4% after 50 cycles (projected 90.8%)
Energy density/ Wh Kg^{-1}	-	185	196.9
Average voltage output/ V	2.2	3.4	2.93

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Table 4

	PPQs	Activated carbon	MOFs/Graphene
Average specific $mAhg^{-1}$ capacity after applied a current density of 500 mAg^{-1}	1	2	3
Cycling stability	3	2	1
Energy density/ $Whkg^{-1}$	2	2	3
Average voltage output/ V	1	3	2
Total	7	9	9

3. Discussion

An analysis of organic-based sodium ion batteries in comparison to lithium ion batteries

Section 3 of the literature review has provided a detailed overview of three main pieces of pivotal information which will be used in this discussion: the synthesis methods of each organic material, electrochemical analysis, and the disadvantages associated with each type of organic material. These three key indicators are crucial because they provide a quantitative basis for the evaluation of each material in terms of performance, sustainability, and economic viability, the main evaluation criterias to fabricate a successful battery. By the end of this section, the improvement of organic batteries in recent decades will be evaluated against that of lithium ion batteries to show the potential replacement of lithium ion batteries by organic-based sodium ion batteries.

Since the electrochemical analysis varies greatly between each paper, the evaluation matrix of batteries must change to accommodate the existing data. To assess the potential for lithium ion batteries to be replaced by organic batteries, three main factors need to be considered, including performance, sustainability and economic feasibility. Although the variable that is being considered is different from our first evaluation in 'The Current Technologies' section, the main evaluation criteria of capacity, power output, safety, and durability remains unchanged. In this discussion section, there will be two main comparisons made between lithium cobalt oxide batteries and metal-organic framework/graphene batteries, and lithium cobalt oxide batteries and activated carbon batteries.

Table.3

	Lithium Cobalt Oxide	Activated carbon	MOFs/graphene
Average specific mAhg-1 capacity after applied a current density of 500 mAg^{-1}	850	265	402
Cycling stability	96% after 50 cycles (projected 92% after 100 cycles	93% capacity retention after 100 cycles	95.4% after 50 cycles (projected 90.8% after 100 cycles)
Energy density/ $Whkg^{-1}$	300	185	196.9

Average voltage output/ V	3.6 - 3.9	3.4	2.93

4.1 Performance:

In similar fashion to the comparison of ‘current technologies’ and ‘rising technologies’, the performance of lithium-ion batteries and organic batteries will be compared through three prevalent indicators: power output, durability, and safety. This covers a broad range of electrochemical performance which is relevant to modern electrical applications. I will discuss, based on quantitative data to ensure objectivity, the electrochemical performance of each battery in the literature review.

Power output and capacity:

LCO batteries show the most promising result at the current stage of battery development as they contain the highest average specific capacity of 850 mAhg-1 upon the application of a current density of 500 mAg-1, compared to the 265 and 402 mAhg-1 of activated carbon and MOFs/graphene, respectively. In other words, LCO contains more electric charge per gram of the battery itself, which allows them to produce greater current discharges for longer amounts of time. These results coincide with the energy density shown on table.3, where LCO contains the most energy density of 300 Wh Kg-1 out of the three.

This is pivotal for applications in devices that require extended use of batteries with high energy consumption such as laptops. These results, although much expected from its widespread use, rooted from the fact that lithium-ion batteries have been industrialised for longer and were widely researched since its introduction in the 1970s[55], whereas sodium-ion batteries were released a few decades later [56]. Fundamentally, if researchers direct their focus towards organic-base sodium batteries and given the same development timeframe as LCO batteries, the ‘rising technologies’ should drastically improve in terms of power output and energy capacity.

(1) Power density = (Voltage × current) / (kg)

As shown by equation (1), power density is directly proportional to the voltage. Therefore, batteries with higher average voltage output tend to contain greater power density. From table.3, LCOs exhibit the greatest voltage between the electrodes of 3.6-3.9 V compared to those of activated carbon and MOFs/graphene of 3.4 and 2.93 V, respectively. LCO’s high voltage, thereby, alludes to greater power output. Since lithium-ion batteries are widely used in energy-demanding applications, the replacement of such batteries requires batteries with high power density as well. From the data shown, the small gap between the voltages of LCO and organic-based batteries are small, which suggests that the latter can be applied in similar applications as well.

Durability:

Additionally, by evaluating cycling stability statistics, the rate of battery decay over an extended period of use is compared, demonstrating a rate of decline in performance. All three batteries show very similar rates of decay as LCO has a capacity retention rate of 96% after 50 cycles; activated carbon contains 93% capacity retention rate of 100 cycles; and MOFs/graphene contains a retention rate of 95.4% after 50 cycles. However, since there is a lack of data for the capacity retention at the 100th cycle for LCO and MOFs/graphene batteries, I assumed that LCO and MOFs/graphene at the same rate until the 100th cycle, allowing me to fairly compare the cycling stability of all three technologies at the 100th cycle.

By calculation, the estimated capacity retention rate of LCO and MOFs/graphene batteries will be 92% and 90.8%, respectively, which are both lower than that of

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activated carbon. Thus, activated carbon batteries excel in this aspect, containing a higher charge-discharge cycle with less capacity degradation, or what is widely known as ‘capacity loss’. In real-world applications, activated carbon batteries do not have to be changed as often as the other two, but these slight differences between capacity retention does not create a massive difference in battery life. Hence, it is safe to assume that all batteries are applicable in modern day electrical appliances.

Overall performance:

Despite LCOs topping almost all of the performance evaluation criteria, the other two technologies are not significantly worse, especially in average voltage output and cycling stability, where activated carbon exceeds LCO technology. Not to mention, the two organic batteries is based on a sodium-ion mechanism, which, electrochemically, is already inferior to lithium ion because of sodium-ion’s larger ionic radius and higher ionic mass hinders diffusion rate, resulting in poor energy density and cycling stability[57]. Hence, with further research on intercalation issues of sodium-ion in cathodes, organic-based batteries already show the potential to replace cobalt oxide cathodes in terms of performance.

Sustainability:

As mentioned in earlier sections, sustainable batteries are becoming increasingly prevalent in the modern day industries. Unethical exploitation of workforces, environmentally damaging raw materials sourcing methods, and resource depletion are the major concerns which drove the urgency for such this transformation. To fully evaluate the sustainability of each battery material at a great depth, discussing whether each technology can be longstanding or not, this section is separated into four main fragments: sourcing of raw materials, disposal hazards, recyclability, and labour exploitation.

Sourcing of raw materials:

In light of raw material sourcing, activated carbon is the most beneficial and environmentally friendly approach out of all three technologies. Despite its high temperature conditions required for calcination as shown in section 3, the synthesis of activated carbon is from the conversion of waste biomasses into a higher value-added product, both reducing the waste inside landfills which produce methane (a greenhouse gas) and mitigating exploitation of natural resources[58]. From the literature review, the chosen precursors of rice husk is a widespread agricultural waste that can be easily sourced and transported across the globe. Hence, obtaining rice husks as a raw material in industries are easily implemented and require few extra materials preparation steps which does not heavily require other resources.

With MOF/Graphene batteries, Molybdenum is the 58th most abundant material on the Earth’s crust, and it will not run out in the foreseeable future[59]. Also, selenium can be easily obtained from the by-product of copper ore extraction. On the other hand, modern graphene synthesis methods used to form nanocomposites with the abovementioned alloys are unsustainable due to intensive mining of graphite and use of N,N-dimethyl-formamide (DMF); N-methyl-2-pyrrolidone (NMP); dichlorobenzene (DCB), which are highly toxic chemicals[60]. The extraction of molybdenum suffers from the environmental impacts of mining, similar to that of

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lithium[61].

For LCO batteries, lithium extraction has widely been regarded as dangerous to the environment. Firstly, approximately a third of the world's Lithium metal sources come from salt flats in Argentina and Chile where large volumes of water are exploited to mine these ores in such arid areas, meaning an increase in ore extraction in the future can result in regional water shortages. This exacerbates food shortages in underprivileged communities as there are not enough water resources to irrigate crops, potentially leading to widespread starvation.

Disposal and recyclability:

Activated carbon, yet again, excels the most in this evaluation criteria. After repeated uses of its properties as an electrode material, the continuous intercalation-deintercalation of large sodium ions (as used in literature review) creates constant mechanical stress and irreversible physical changes to the carbon. However, the reactivation of activated carbon can diminish the faults created, allowing the unfunctional activated carbon to be recycled with low cost while using environmentally friendly materials such as potassium hydroxide[62]. By continuously reactivating the carbon, despite the small drop in electrochemical performance in each cycle, activated carbon can be easily recycled which is extremely useful when sourcing raw materials.

In addition, MOF/Graphene's electrodes are also safe to dispose of relative to both activated carbon and LIBs. Graphene exhibits, effectively, the same structure to activated carbon as they both consist of elemental carbon. Because of this, graphene exhibits low toxicity and is unlikely to cause harm to the environment upon disposal. Also, molybdenum is vastly recycled in the modern world[63]. Therefore, this metal is rarely inputted into landfills as waste, producing small disposal footprints. To my knowledge, the non-toxic nature of graphene, intertwined with the fact that molybdenum and selenium are fully recyclable[64], ensures that SIBs based on MOF/Graphene electrodes can be safely disposed and recycled to mitigate further resource depletion.

On the other hand, the lack of proper LIB disposal is one of the key factors this dissertation aims to tackle. As mentioned previously in Section 2, the high associated energy and challenges in recycling lithium and cobalt metal repels organisations to recycle LIBs. This is heightened by the fact that the polymeric membranes and electrolytes used in these batteries are highly toxic to the environment. Furthermore, cobalt is a highly toxic metal that causes severe poisoning. Hence, according to all of the information provided in the literature review, I can safely assume that the production and disposal of LIB are not sustainable, both environmentally and socially.

Overall evaluation of sustainability:

Assessing the factors of sourcing, disposal, and recyclability of each type of battery, it is clear that activated carbon excels in sustainability most. Though MOF/graphene's electrodes are generally safe to dispose of, mitigating the issues of unsafe battery disposal, the synthesis of activated carbon is much more effective as it solves three issues simultaneously: waste management, safe disposal, and resource depletion. The substance is derived from agricultural wastes such as rice husks, reducing wastes going into landfills and decreasing the need for rare earth metals such as cobalt (used in LCO batteries) to be extracted. Hence, activated carbon batteries are one of the most environmentally friendly alternatives to LIBs.

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***Economic* viability:**

Not only do successful batteries possess exceptional power output, capacity, and environmentally consciousness but they must be scalable for industries throughout the world, if they were to replace lithium ion batteries. In this subsection, scalability will be predominantly discussed in detail since it is the main limiting factor to the development of 'Rising technologies.' The cost of production plays a large role in the scaling process. As aforementioned, I have chosen SIBs in MOFs/graphene and activated carbon will be cheaper than LIBs because sodium is much more abundant than lithium, and sodium can be extracted from the ocean.

Since lithium is already sold on an international scale with ever increasing demands, it has already proven the massive potential for scalability.

For MOFs/graphene batteries, even though molybdenum is widely used as lubricants[65], selenium and graphene are scarce. First, selenium is a rare earth element and is often found in copper and lead ores from mines. Consequently, a series of purification stages need to be completed to form a selenium element. Also, monolayer graphene costs over $100,000/kg[66] because graphene synthesis methods include sophisticated processes such as chemical vapour deposition or ultrasonication. Not only are they expensive but they also produce very small masses or even small flakes of graphene which are not adequate for industrial applications. There are also no machines which can produce large sheets of graphene which further limits the scalability of MOF/graphene batteries. Hence, this organic battery technology, although it remains a great alternative in terms of performance and sustainability, can only be economically viable if graphene can be produced in large quantities at significantly lower costs.

Activated carbon electrodes cost very little to produce because most precursors are derived from biowastes. Rice husk precursors can cost as low as $3.58-3.77/kg, which allows for battery production to be purchased in bulks[67]. But with such benefit comes a limitation such that biowastes show very little product consistency and high purification needed for industrial use. Also, high temperatures are needed for carbonisation stages such as hydrothermal carbonisation, calcination, and pyrolysis which is energy intensive and drastically increases the demands for fossil fuels so mass production of activated carbon will contribute to enhanced greenhouse effect. Also, since most of the rice husk comprises a lignocellulosic structure, the high thermal treatment causes it to decay significantly, reducing the yield greatly. This massive loss in product can potentially create bottlenecks in industries. However, this can be mitigated by adding rice husks at a greater rate, which is possible due to the low cost nature of the raw material.

4.3.1 Overall economic viability evaluation:

Overall, although LIBs have been manufactured across the globe due to its exceptional scalability, activated carbon is a prospective electrode material that is both cheap to manufacture and it can be sourced locally through agricultural wastes. With further research and development in maintaining raw material consistency in rice husks, activated carbon could potentially match the global scale LIBs have reached.

Conclusion

Incorporating all three factors of performance, sustainability, and economic viability into account, we can conclude that hybrid organic sodium ion batteries

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can replace modern day battery technology to some extent. Research papers have demonstrated that while the hybrid battery cannot outperform the lithium ion battery in terms of power output and capacity, it exhibits a cycling stability that is similar or higher than that of lithium cobalt oxide batteries. Activated carbon batteries appear to contain more desirable properties than MoSe2/graphene batteries because of their higher energy density, average specific capacity, and cycling stability. Therefore, it will be considered for this conclusion. Since it mitigates both waste management and depletion of transition-metal materials, the precursor materials can provide significant environmental benefits. Additionally, the electrochemical performance of the hybrid batteries is nearly comparable to that of lithium batteries, allowing them to be used in low power-demanding applications such as mobile phones and other portable devices.

On the other hand, this battery was only tested once on a lab scale as presented on the paper so it will be challenging to assume that the electrochemical performance and consistency will remain on an industrial scale. Additionally, the sourcing of raw material in activated carbon is a double-edged sword, wherein it solves wastage problems but also reduces scalability due to the low product consistency of wastes. However, this problem is mitigated by using rice husk as a precursor because it is extremely abundant across the globe as waste so it is cheap through to purchase, making rice husk activated carbon become a very feasible alternative to lithium ion batteries parallel to the increasing ethical and environmental concerns of the latter battery production.

In conclusion, sodium batteries hybrids with activated carbon electrodes have significant potential to be mass produced and applied into low-power consumer electronics today. As shown by the electrochemical performance and the synthesis procedures as discussed above, these hybrid batteries can be named an alternative to lithium batteries. We, however, cannot be certain whether it would bring comparable scalability to the latter type since there is no further research on the production-scale applications. In the foreseeable future, researchers should test out the rice husk battery on a large scale, and find other chemical activators to further increase the microporosity of activated carbon to increase surface area for redox reactions at the battery's electrode. This will further heighten the performance of the sodium ion hybrid battery.

Through the intersection between materials and energy, researchers have begun to realise the importance of developing energy storage systems using renewable materials, which is the sole focus of this research. With the aim to eradicate massive amounts of rare earth metal extraction and harmful waste disposals created by the implementation of lithium-ion batteries, the solutions presented in this research simultaneously mitigates these issues. Activated carbon, specifically, can be readily implemented by current sodium-ion batteries today, with adequate electrochemical performance and cheap sourcing of raw materials. In addition, carbon can be tailored to many versatile applications in energy uses including (but not limited to), supercapacitors, photovoltaic cells, electric motors. Hence, sustainable organic batteries have the potential to revolutionise energy storage by offering a more environmentally and versatile alternative to conventional batteries. As research and development in organic batteries continue to progress, this research is bound to be a crucial source of information from which researchers can benefit, contributing to the rise in a more resilient global energy structure.