Consilience: The Journal of Sustainable Development
Iss. 26 (2022-2023)

CONSILIENCE

THE JOURNAL OF SUSTAINABLE DEVELOPMENT

Comparing Sodium-ion Battery Electrode Materials in the Scope of Grid-Scale Batteries supporting Renewable Energy Sources and Future Electrification Demands

Aryan N. Saha
Kent School

Abstract

With current emission outputs from electricity generation, multiple stakeholders seek to decarbonize and transform current energy grid technology and energy generators. In support of this transition, this paper analyzes the technological capabilities of current grid-scale level energy storage systems and provides a process of prioritizing electrode material qualities. In specific, this paper explores anode and cathode materials for Sodium-ion batteries utilizing attributes oriented for energy grid usage. This paper proposes the weighted-ranking system considering factors of reversible capacity, energy density, cycling ability, and material abundance. This paper seeks to aid those researching future electrode materials for SIBs in the context of future grid-scale level batteries through contextualizing various electrode materials in comparison. This paper also seeks to provide a valid method of comparing multiple electrode materials to recommend specific research and development areas.

Keywords: Sodium-ion batteries, lithium-ion batteries, energy storage, grid systems, renewable energy.

I. Introduction

1.1 Status Quo and Future of Energy and the Grid

Through the IPCC's AR6 report, the panel states how warming of the Earth to 1.5℃ would cause "unavoidable increases in multiple climate hazards and present multiple risks to ecosystems and humans" through climate change" (Pörtner et al., 2022). Due to the harmful effects of climate change, researchers, politicians, activists, and general citizens seek to decrease the cause for global warming: greenhouse gases, such as CO_2, which are able to retain heat energy within the atmosphere and warm the planet. Reducing greenhouse gas emissions is key in order to prevent the catastrophic consequences of global warming.

Within the United States, the electricity sector emitted 1,482 million metric tons of CO_2 in 2020. Fossil-fuel generation sources are largely to blame. Natural gas, coal combustion, and petroleum account for 60% of U.S. electricity generation, with 54% of CO_2 emissions from this sector coming from coal combustion alone (Sources of Greenhouse Gas Emissions, 2021). In addition to this, energy demand is increasing. According to the International Energy Agency, energy demand is expected to increase by 4-5% in the coming years (Global electricity demand is growing faster than renewables, 2021). Thus, attention is drawn towards how to shift the current electrical grid, based on non-renewable energy generators, to a decarbonized and expanded future power grid utilizing alternative energy methods.

1.2 Renewable Energy and Electrical Grids

As to be explored in later sections of this study, typical energy production systems do not depend on natural inputs, unlike most renewable energy sources. Because of the manual control of fossil-fuel and coal-based electricity generators, current day electrical grids are adapted to a certain amount of navigability in terms of energy production and handling. Due to the variable nature of certain energy sources, such as wind and solar which are dependent on natural circumstances, researchers and grid managers are growing in interest in utilizing energy storage systems–both to handle variations in electricity and energy demand, as well as providing for added energy security. Various forms of energy storage approaches, such as "secondary battery technologies, flow batteries, supercapacitors, flywheels, compressed air energy storage, thermal energy storage, and pumped hydroelectric power" are both implemented and in investigation for implementation (Fan et al., 2020). Within the scope of electrical energy grids, battery technologies are highly considered as a preferable option, due to their "modularization, rapid response, flexible installation, and short construction cycles" (Yabuuchi et al., 2014). As such, current research and development in battery systems consider handling specific needs of future energy grids. With such variation in current available technology, it can be difficult to assess current solutions given the next century's environmental, economic, and political contexts. Successful solutions to our current electrical grid and energy storage dilemma would allow for rapid growth and adoption of renewable energy systems, accelerating our pathway to carbon-neutrality. This study aims to explore those parameters within power grids, current electricity storage systems, and other components of electrical energy technology.

1.3 Electricity Management by Power Grids

In the scope of advancing our current grid for decarbonization, the growth of renewable energy has led cause for concern within energy management. As typical energy distribution systems match energy demand with a complex matching of various energy generation sources, the onset of PV energy, wind turbines, and other nature-dependent energy sources decrease our control of managing the supply of energy. As described by Kroposki et al, increasing variable renewable energy (VRE) usage within the energy grid potentially leads to conflicting results, economically. Their study revealed that at an 80% VRE implementation scenario, restricting energy generation from VREs demonstrated the most economically viable solution (Kroposki et al., 2017). This demonstrates how the current energy grid is not optimized for VRE implementation, as demonstrated by its economic inviability.

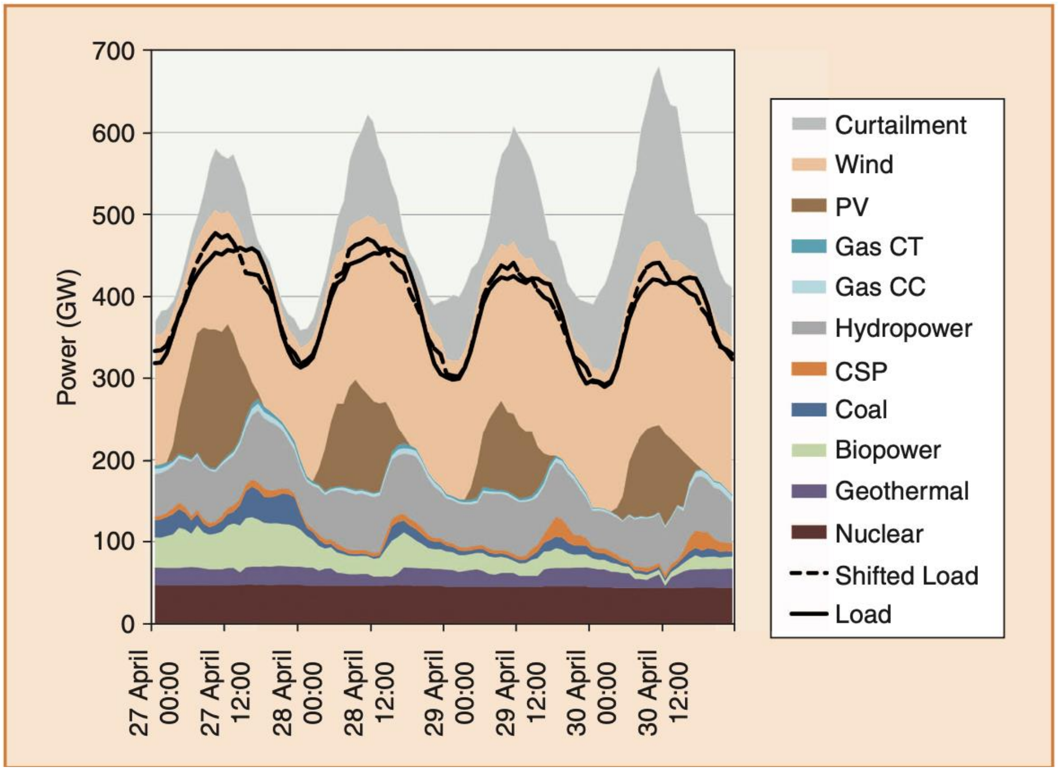

Figure 1: Off-peak production for an 80% VRE transmission-constrained scenario (Kroposki et al., 2017)

Through the added variability of renewable energy sources, grids must change how they adapt to the variable supply. One such method includes Demand Response (DR) (Uddin et al., 2019). Within this process, grid system managers employ a series of schemes in order to decrease electrical energy demand. Most schemes economically incentivize a load reduction from consumers: price-based DR and incentive-based DR. Price-based DR includes time-of-use tariffs, critical peak pricing, and real-time pricing to reward customers' load reduction. Incentive-based DR includes direct load control, curtailable load, and demand side bidding programs to incentivize consumers to reduce load (Paterakis et al., 2017). However, none of these schemes manage how the grid itself adapts to certain energy demand loads. Grid managers may implement a scheme to increase energy capacity through increasing the energy generator usage. This scheme is known to not be "economically feasible and inefficient" (Uddin et al., 2019).

1.4 Energy Storage Systems for Power Grids

With the projected increased demand for electrical energy, these DR systems will not suffice. As a solution, electrical-grid system managers seek to employ an alternative form of demand response: the "Integration of Energy Storage Systems" (Uddin et al., 2019). Energy storage systems (ESS) allow grids to manage moments of stress, in addition to matching energy excess demand with excess supply. Within the context of grid systems, energy storage systems remedy fluctuations of supply and demand through two processes: peak load shelving and load leveling. Within the typical grid cycle, peaks refer to the lowest and highest points of energy demand. Energy storage systems will charge from energy generators during moments of low-demand, whereas ESS will discharge during moments of high-demand. This process of reducing peaks allows for typical on-demand energy generators to reduce the variability of energy production. In the context of variable energy sources (wind, solar), peak load shelving can reduce wasted energy potential, allowing grid-system managers to utilize VREs despite the time of day.

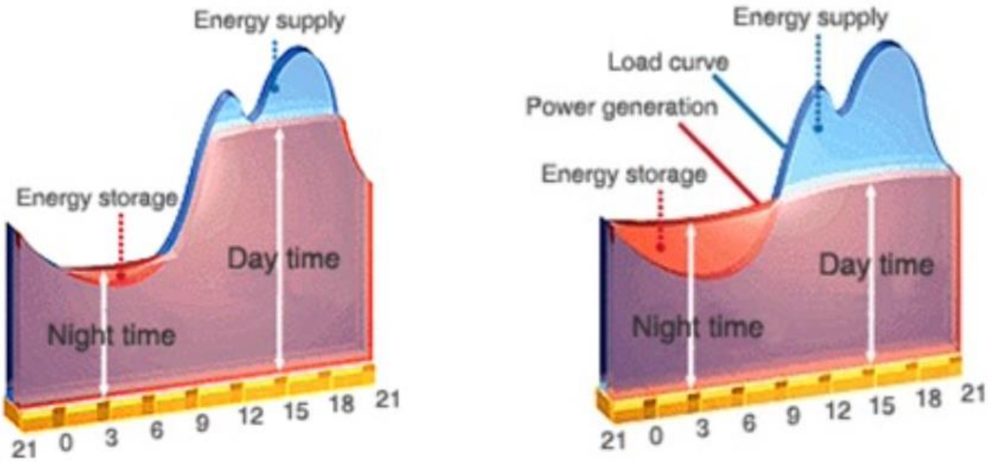

Figure 2: (Fan et al., 2020)

As shown by Figure 2, the ESS will absorb energy from energy supply during low-demand (typically nighttime) as demonstrated by the red, and the ESS will discharge energy to the grid during high-demand as demonstrated by the blue. Load leveling refers to flattening the overall load "rather than simply [removing] the system's peaks". Load leveling allows for economic benefit within the grid (Kerestes et al., 2012). In addition to providing fast "frequency and voltage regulation," battery energy storage systems are a clear possibility to aid the implementation of variable energy sources to our grid (Fan et al., 2020).

1.5 Lithium-ion Batteries

Lithium-ion batteries are well-established as a strong, efficient, and dense energy storage system. Lithium-ion batteries have a "relatively high energy density (up to 200 Wh/kg, with Wh/kg referring to the amount of energy transfer available per kilogram), high [energy efficiency (EE)] (more than 95%), and long cycle life (3000 cycles at deep discharge of 80%)" (Chen et al., 2020). Commercialized by Sony in 1991, Lithium-ion batteries have been at the forefront of battery research (Manthiram, 2017).

Common lithium-ion batteries are based on "insertion-reaction electrodes and organic liquid electrolytes" (Manthiram, 2017). As demonstrated by Figure 3, lithium-ions are rocked back and from either electrode. The cathode consists of a metal oxide, typically of lithium manganese oxide or lithium cobalt oxide. The anode consists of a "graphitic carbon on a copper current collector". The organic liquid electrolyte for lithium-ion batteries are either lithium salts, such as LiPF6, LiN[CF3o2]2, and LiBF4, or lithium bix-oxalato borate LiBOB dissolved in carbohydrate mixtures (Fan et al., 2020).

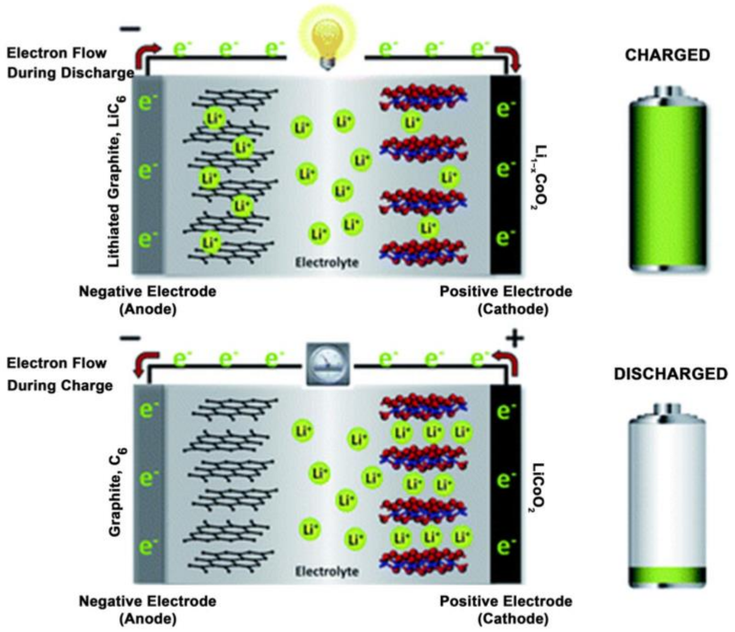

Figure 3: Diagram of Lithium-ion Battery (Kerestes et al., 2012)

1.6 Battery Materials

Grid-scale level energy storage systems require capable energy capacity, high energy efficiency, fast response time, and relatively long lifetime (Chen et al., 2020). As previously noted, lithium-ion batteries store up to 200 Wh/kg, they last around 3000 cycles at an 80% deep discharge and have a high energy efficiency of 95%. For these reasons, lithium-ion batteries have been implemented in 77% of all energy storage systems for grid-scale level batteries (Chen et al., 2020). However, li-ion batteries have various drawbacks preventing them from becoming the sole savior for VRE-powered grids. Lithium exists in relatively low abundance within the Earth, at around 20 ppm. With lithium only found in select countries like South Africa, Chile, and China, li-ion batteries may increase in price. According to Chen et al. , the scarcity of lithium metal causes the high cost, causing doubt and concern for the applicability of grid-scale li-ion batteries (Chen et al., 2020). In addition to material abundance, the geographical deposits of these materials have political implications. Thus, researchers are looking into alternative Electrical Energy Storage systems of matching response time, energy density, and of more abundant Earth materials.

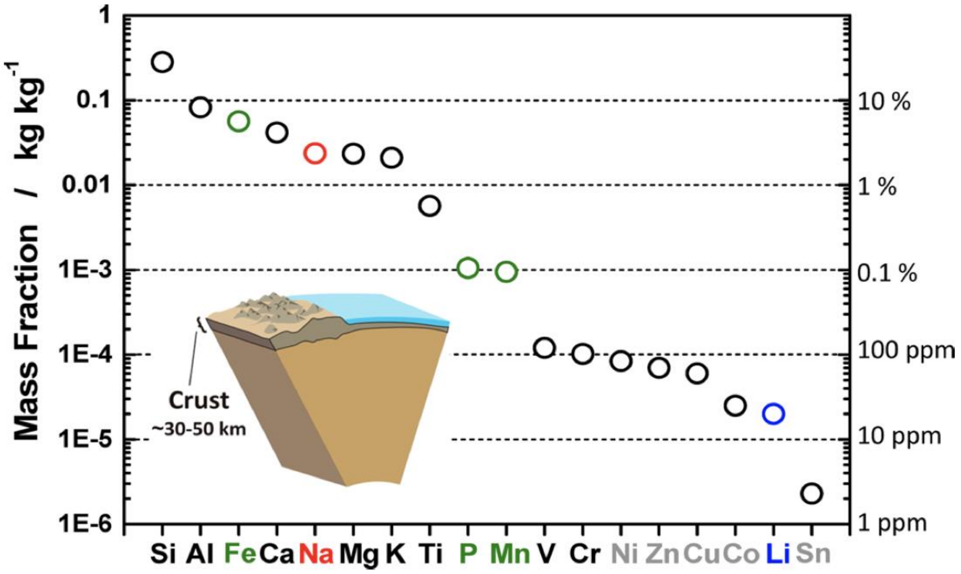

Figure 4: Elements' Crustal Abundance (Yabuuchi et al., 2014)

Through the research of Yabuuchi et al., they've compiled a list illustrating the relative abundance of certain elements within our planet. While lithium correlates more with scarcity, other elements, such as Fe, Na, Ca, and Mg, are far from the rarity of lithium. One common element in particular has strong similarities to lithium: sodium (Nayak et al., 2017). In addition to being the "fifth most abundant element," sodium fits just shy of lithium's championing characteristics (Gür, 2018). Lithium reigns as the battery-element due to its high polarity and low radius (r = 0.59, CN = 4). Within the periodic table, sodium is just one period away. Sodium has less polarity and a larger radius (r = 1.02, CN = 6) (Nayak et al., 2017). Sodium also has a weaker standard reduction potential of -2.7 volts against lithium's -3.04 volts (Pan et al., 2013). As we'll soon explore, many developments aim to decrease the delta between reduction potentials, causing sodium-ion and lithium-ion batteries to exist as complementary.

1.7 Sodium-ion Batteries

Sodium-ion batteries have been investigated and researched at the same rate as lithium-ion batteries from the 1970s to the 1980s (Pan et al., 2013). With lithium-ion's booming success, much research shifted over to lithium-ion battery technology. As previously explained, research is now accelerating in the sodium-ion area due to potential resource challenges in the future. Yet, sodium-equipped batteries are not something of great promise and optimism, Na-S and Na-NiCl2 batteries already exist in commercial form (Pan et al., 2013). Roughly 50 years ago, a "high-temperature solid-state sodium ion conduct - sodium β"-alumina (NaAl11O7)" triggered interest in the area of sodium electrochemistry (Ellis et al., 2013). Since then, sodium-sulfur batteries have been engineered to operate at approximately 300 degrees Celsius, causing both sodium and positive electrodes to become molten. This shift in state of matter allows for the decrease dendite formation, leading to little chance of an internal short circuit (Ellis et al., 2013). However, safety-issues associated with cells operating at such high-temperatures diminish the battery-type's potential for implementation in ESSs.

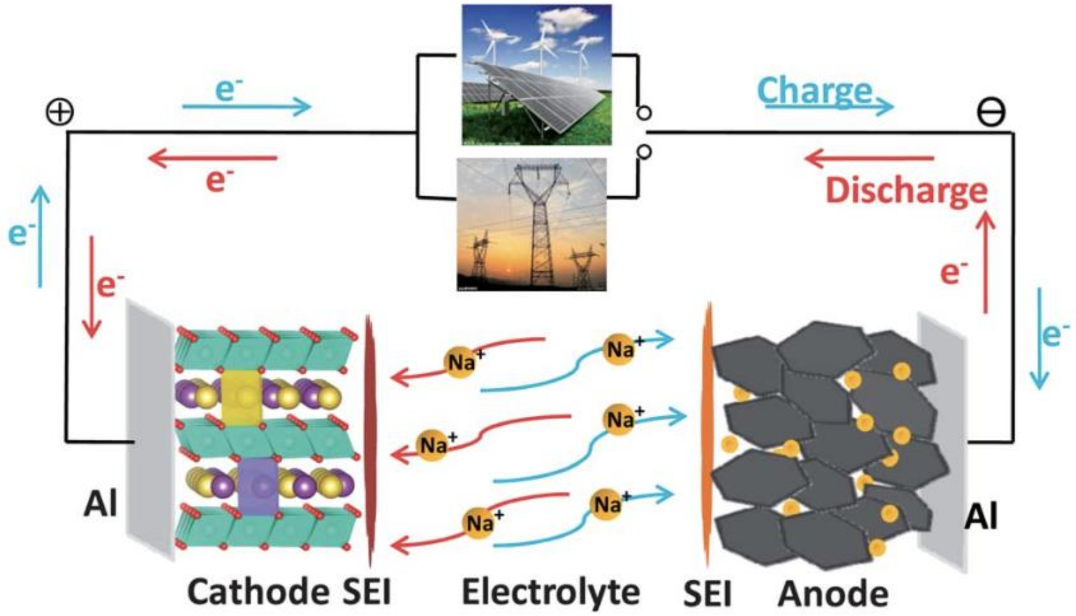

Figure 5: Diagram of Sodium-ion Battery (Gür, 2018)

Per Figure 5, sodium-ion batteries work in a similar system as lithium-ion batteries. The key component of the shuffling-ion exists in both sodium-ion and lithium-ion batteries. When the battery discharges, sodium-ions leave the cathode and intercalate, the process of an ion inserting within vacant spaces in a crystal lattice structure, within the anode. When the battery charges, sodium-ions leave the anode and enter the cathode, thus creating energy potential. Due to the similarity of lithium-ion and sodium-ion batteries, researchers have attempted to engineer sodium-ions off the template of lithium-ion batteries. Both the battery components and energy storage mechanism are similar, with only the "ion carriers" differing between batteries (Hwang et al., 2017). As researchers are using the template of lithium-ion batteries, most areas of research involve adapting an electrode material, electrolyte, or current collector to better work with sodium-ions.

Ever since the 1980s, researchers have developed intercalation materials using non-aqueous electrolytes, just like lithium-ion batteries. Despite the similarity of intercalation chemistry, the replacement of sodium with ion requires heavy research into "new electrode materials" and new "stable electrolytes" (Ellis et al., 2013): the increased radius of sodium compared to lithium, along with other aspects, decreases its ability to intercalate at electrodes. Much of cathode materials have been mimicked from lithium-ion batteries. Sodium-ion intercalation materials were explored by Whittingham and Hagenmuller around the 1970s and 1980s; they proposed sodium intercalation into layers of "MoS2, TaS2, TiS2 and NaxMO2" for cathodes (Pan et al., 2013). Anodes, on the other hand, present more issues. Within li-ion batteries, the anode consists of graphite to allow for lithium to intercalate. Due to the energetic instability of Na-GIC (Sodium intercalated in graphite), sodium-ions cannot intercalate with graphite (Hwang et al., 2017). Commonly used in laboratories, metallic sodium is not optimal as a production-level anode due to its dendrite-formation causing safety and cycling issues (Li et al., 2017). Hence, researchers prioritize discovering suitable materials, such as carbonaceous materials, to create cost-effective and high-voltage sodium-ion batteries. Companies such as CATL and Fardion have already demonstrated exceptional prototypes of non-acqueous sodium-ion batteries. CATL produces sodium-ion batteries, utilizing Prussian white for the cathode and a porous hard carbon for the anode. Through their research, they have achieved up to 160 Wh/kg, nearing the energy density of lithium-ion batteries, and the ability to charge to 80% within 15 minutes (CATL Unveils, 2021). Fardion has achieved 160 W h kg^-1 in 32 A h pouch cells at 4.2–1 V (Rudola et al., 2021).

1.7.1 Sodium-ion Cathode Materials:

1.7.1.1 Layered Oxides

One of the most promising cathode materials for increased capacity, safety, and response for grid management includes layered oxides, noted as the "most extensively studied cathode" due to their research-conception in the 1980s (Li et al., 2017). Delmas et al. studied layered oxides of the structure A_xMO_2, with A being an akali-metal ion and M being a transition element with two oxidations states (Delmas et al., 2021). Layered oxides are defined as the "crystal structure of layered compounds" which depends "on the stacking sequence of alkali ions between layers". Within the context of sodium-ion batteries [SIB], the two-dimensional layered-oxide empirical formula is $Na_{1-x}MO_2$ (Hwang et al., 2017). These layered-oxides are, of course, modeled from common lithium-ion battery cathodes. What usually takes the shape of LiMO2 (M = Co, Mn, Ni, etc.), takes the shape of NaMO2 (Ellis et al., 2013). According to Delmas et al. , sodiated transition metal oxides come in two key formations: O3 and P2. "O3 " represents octrahedral (O) crystal structures containing three sodium-ions. “P2” represents trigonal prismatic (P) crystal structures containing two sodium-ions (Li et al., 2017). These octrahedral or trigonal prismatic environments represent the structure of the layered oxide, as demonstrated through Figure 6.

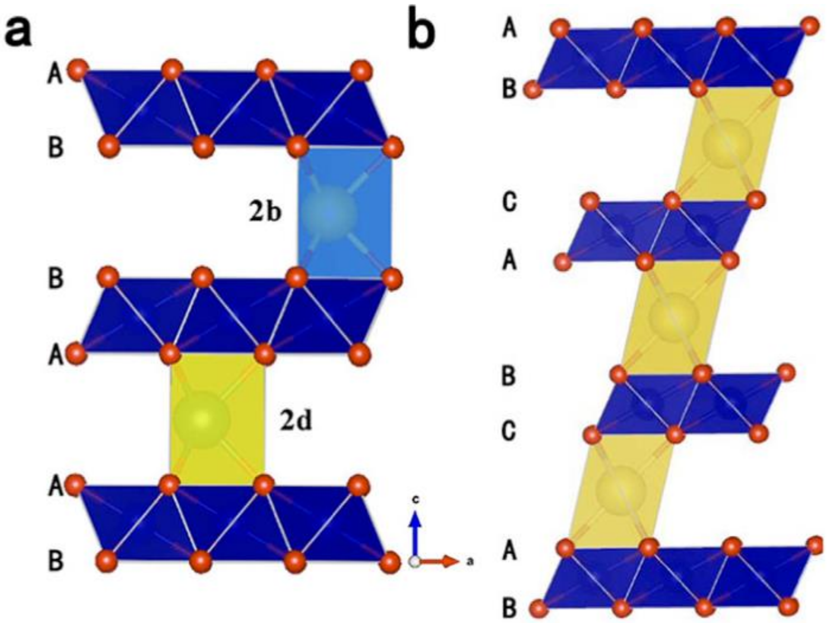

Figure 6: (Left) P2 formation (Right) O3 formation
(Li et al., 2017)

As demonstrated by Figure 6a, a P2 formation includes an alkali-ion in 2b or 2d. As demonstrated by Figure 6b, an O3 formation includes an alkali-ion in three various areas. In addition to differing ion-storage quantities, these different structures alter multiple characteristics: capacity, cyclability, energy density, etc. Within these cathodes, Na will intercalate with the layered oxide materials in either an O3 or P2 formation. Formations indicated such as O'3 or P’3 indicate a monoclinic distortion, simple alterations to the structure, to the original phase (Hwang et al., 2017). According to Hwang et al., O3 formations become stable with higher concentrations of lithium. For sodium-ions entering an O3 formation, such a crystal structure will enter phase changes of O3 ↔ O’3 ↔ P3 ↔ P’3. Hwang et al. states how P2 crystal structures are most stable with “Na content” in the “range of 0.3-0.7” (Hwang et al., 2017). As researchers seek to discover layered metal oxides with a reversible capacity, the energy quantity that can be lost through discharging and later recovered through charging, of >200 mA h g^{-1} at an average potential greater than 3.0V, researchers are wary of the typically associated pitfalls of these cathode materials. Such issues include “structural instability due to multiple phase transitions and structural variations during Na-insertion/extraction,” a process which typically results in capacity decay (Qian et al., 2021). Notable sodiated transition metal oxides include $NaCoO_2$, $NaCrO_2$, $NaVO_2$, and $NaMnO_2$.

$NaCoO_2$

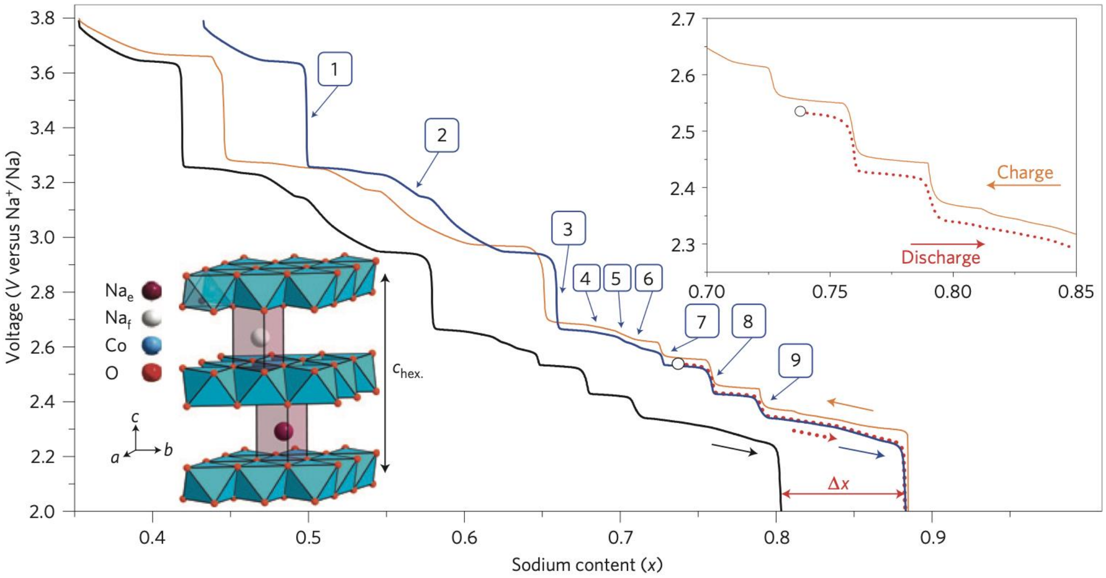

Figure 7: Source (Chromium, 2022)

$NaCoO_2$ was first analyzed by Delmas et al. as they illustrated the sheet phases of the oxide. $NaCoO_2$ can extract up to “0.5 Na with multiple plateaus in the electrochemical curve.” According to Delmas et al., cathodes starting with P2-$Na_{0.77}CoO_{1.96}$ yield a 230 Wh/kg theoretical energy density (Delmas et al., 2021). Cathodes starting with P2-$Na_{0.70}CoO_{1.96}$ yield a 260 Wh/kg theoretical energy density (Li et al., 2017). While the relatively high energy density portrays $NaCoO_2$ as a plausible choice for a SIB cathode material, the usage of Co is associated with availability issues. However, with abundance on par with Lithium, at 26.6 ppm, utilizing a cobalt-based cathode would solve little resource issues (Cobalt, 2022).

$NaCrO_2$

Like other layered oxides, $NaCrO_2$ compares against $LiCrO_2$. Unlike other layered oxides which simply replace a successful cathode material with a layered sodium oxide, $NaCrO_2$’s qualities are superior to its lithium alternative. Due to the “movement of formed Cr^{6+} to a T_d site,” layered $LiCrO_2$ cannot reinsert Li after extraction and is therefore electrochemically inactive. Within $NaCrO_2$, Cr-ions stay in layered oxides’ transition metal layer after Na extraction (Li et al., 2017). In addition, Na-ions are thought to diffuse faster than Li-ion in the oxide framework due to longer alkali-oxygen bonding in $NaCrO_2$ than $LiCrO_2$(Komba et al., 2021). $NaCrO_2$ has a phase transition of O3 to P3-type structures. This transition metal oxide has an initial discharge capacity, the amount of energy dispelled by the battery in its first cycle, of 120 mAh g^{-1} with a 3.0V operating potential (Ellis et al., 2012). Unlike cobalt, the key transition metal, chromium has an abundance of 126 ppm within the planet (Chromium, 2022). Although not comfortably abundant, chromium is less likely to cause resource issues as lithium or cobalt are.

NaVO$_2$

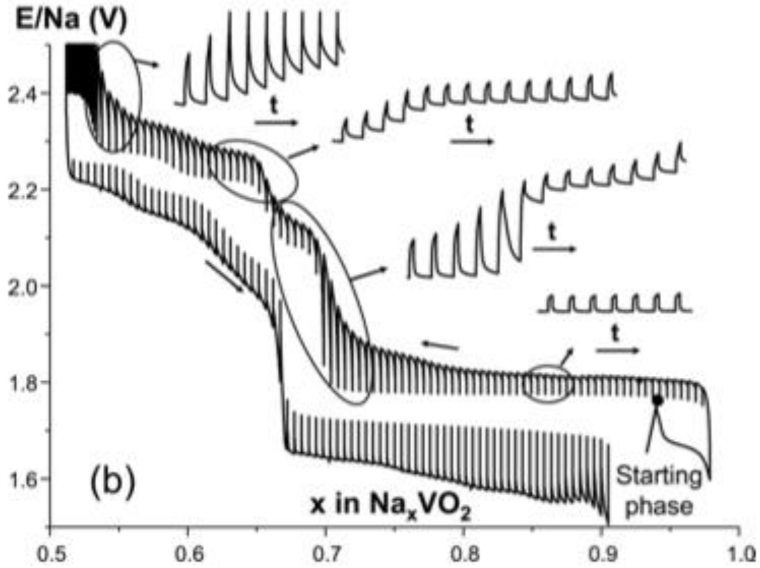

Figure 8: Na_xVO_2 Voltage Graph (Berthelot et al., 2010)

$NaVO_2$ has a reversible capacity comparable to $NaCrO_2$ of 126.4 mAh g^{-1} within a range of 1.4-2.5 V (Shiiba et al., 2013). However, $NaVO_2$ can only be reversible for up to 0.5 mol Na-ion per mole of $NaVO_2$. As determined by Dider et al., this electrode material faces "large voltage variation during cycling" and "oxygen senstivity$_2$. Although vanadium exists at 138 ppm, the low voltage and various issues demonstrate the low practicality of this material (Vanadium, 2022).

1.7.1.2 Prussian Blue and Analogs

Prussian blue [PB] and its analogs' open cubic framework and "favorable interstitial sites" allows for reversible insertion and deinsertion of alkali ions. Prussian blue analogs [PBAs] have the structure of AxMM'(CN)6 (A = Na, K; M and M'=Fe, Co, Mn, Ni) (Li et al., 2017). These compounds are a large family of "transition-metal hexacyanoferrates" with plentiful redox-active sites, stable and strong structure, along with an open framework (Cobalt, 2022). Within the lattices, PBAs have large ionic channels and interstices which allows Na^+, a large alkali cation, to have reversible and facile insertion reactions. The large and spacious structure of PB allows for a diffusion coefficient of 10^{-9} to 10^{-8} cm^2 s^{-1}, signifying high ionic conductivity relative to other insertion cathodes. Each Prussian Blue molecular formula contains two redox centers: Fe $^{+2/+2}$ and $M^{+2/+3}$. Thus, each mol of PB can hold 2 Na^+. From the analysis of Qian et al., "Na_2FeFe-PB can release a considerably high capacity of ≈160 mA h g−1 at average high potential of 3.1 V and Na_2MnMn-PBA can reach a high reversible capacity of 209 mA h g−1 at high potential of 3.50 V (vs Na/Na+)" (Qian et al., 2021). Current research varies the structure and transition-metals of PBs and PBAs, seeking to discover superior capacity, energy density, and cycle life. Of the two redox metals, battery engineers can vary the transitional metals to ones with ample scarcity. Such an example includes the Na_2MnMn-PBA who's transition-metal, Mn, has a crutsal abundance of 774ppm (Manganese, 2022).

1.7.1.3 Phosphates

In the scope of grid-scale level electrical energy storage systems, future sodium-based cathode materials must have comparable energy density, capacity, and structure to depict SIB as a valid choice. Prussian blue and Prussian blue analogous have been described to have high potential for success in each of these qualities. The cubic framework of the material allows for expansive space for Na-ions. Current research has demonstrated possibilities for high reversible capacities. However, conventional synthesis "always exhibits large amounts of vacancies in the crystal framework because of a rapid precipitation process" (You et al., 2014). Due to this, researchers have paid additional attention toward phosphate framework materials as promising cathode materials. As described by Fang et al., strong P-O covalent bonds , found in PO_4^{3-} within phosphate framework materials, can stabilize the lattice oxygen even at a highly charged state. Phosphate framework materials' structural stability allows for safety and long-term cycling. The 3d framework allows for less volumetric expansion and phase transition during insertion and de/insertion of Na-ion. Despite these numerous advantages of phosphate framework materials, the large size and isolating nature of PO_4^{3-} cause low electron conductivity and moderate capacity. Within Lithium-ion batteries, olivine $LiFePO_4$ is a common and "successfully commercialized" cathode material (You et al., 2014). Its sodium analogue, $NaFePO_4$ is known to be more "thermodynamically stable" (Li et al., 2017). As achieved by Liu et al., their NaFePO4@C electrode reached 89% capacity retention over 6300 cycles with a high reversible capacity of 145 mAh g^{-1} at 0.2 C (Liu et al., 2014).

1.7.2 Sodium-ion Anode Materials:

1.7.2.1 Carbonaceous Materials

Within Lithium-ion batteries, anode materials commonly consist of graphite. Due to the smaller size of lithium-ions, they are "readily inserted into graphite with a final stoichiometry of LiC_6, which is equivalent to a capacity of 372 mAh g^{-1}"(Li et al., 2014). As previously noted, sodium-ions have differences from lithium-ions, quite notably the larger ionic radius. When Na^+ is inserted into graphite, the process is significantly impeded with electrolytes/electrodes undergoing degradation (Hwang et al., 2017). In order to solve this issue, researchers take two approaches: expanding graphene layers and utilizing Na^+-solvent co-intercalation (Li et al., 2017). Through the work of Wen et al., they expanded graphite layers from 0.34 nm to 0.43 nm, reaching promising results.

1.7.2.2 Graphitic Materials

The expanded graphite (EG) had a 73.92% capacity retention rate after over 2,000 cycles. EG also provides reversible capacity of 284 mA g^{-1} at 20 mA g^{-1} density (Wen et al., 2014). Expanded graphite was produced through a two-step oxidation-reduction process. As noted by Wen et al., the expanded graphite necessitated at least 0.37 nm of an interlayer distance in order for Na^+ insertion. Corresponding to the second method of utilizing graphite, Jache et al. demonstrate a process known as co-intercalation to create ternary GICs (t-GICS), producing graphite anodes which have high reversibility and cycle life. t-GICs are produced through reducing graphite, allowing for the intercalation of solvated alkali ions, in this case sodium. Equation (1) illustrates the reduction of graphite, with A^+ being an alkali metal, solv being a solvent molecule, and C_n being *n* carbon atoms within the graphite lattice (Jache et al., 2014).

$$C_n + e^- + A^+ + ysolv \leftrightarrow A^+(solv)_y C_n^-$$

Equation 1: Source (Jache et al., 2014)

Through co-intercalating solvent molecules, the issue of sizing between Na-ions and graphite lattices can be resolved. This process utilizes an ether-based or diglyme-based electrolyte to allow for co-intercalation. Both electrolytes allowed for graphite to have an “excellent cycling ability” paired with a relatively high reversible capacity of 150 mAh g^{-1} for ether-based and 100 mAh g^{-1} for diglyme-based electrolytes (Li et al., 2017).

1.7.2.3 Non-Graphitic Materials

Hard carbon, also known as non-graphitic carbon, is the other carbonaceous anode material in heavy research for a promising cathode material. Hard carbon and graphite differ in terms of how Na^+ intercalates with the material. Within graphite, graphene layers are spaced to create a structure of which Na-ions can intercalate. Hard carbons consist of “randomly distributed turbostatic domains with graphene nanosheets and expanded interlayer spacing” (Xiao et al., 2018). This creates molecular complexity in terms of how Na^+ intercalates with the material. A model known as the “card-house” model illustrates a method of how Na-ion’s intercalate into hard carbon (Luo et al., 2014). According to the analysis of Xiao et al., hard carbon materials consist of three types of ion-storage sites within the “card-house”. The first includes intercalations between “graphene sheets in turbostratic graphitic structures". The second type involves storing ions within micropores found in between hard carbon microstructures. The third being through surface and defect absorption (Xiao et al., 2018). Overall, hard carbons are noted to have high reversible capacity and low voltage. Where they potentially bring disadvantages, is in the realm of materials costs. Certain hard carbon material sources, such as biomass and resin, can require “high preparation cost and relatively low carbon yield”, thus driving the cost of hard carbon very high (Li et al., 2017). Stevens and Dahn first demonstrated a glucose-derived hard carbon in 2000, reaching a reversible capacity of 300 mAh g^{-1} (Stevens et al., 2000). Since then, numerous research efforts on hard carbon usage as an anode have occurred. As best reviewed by Li et al., hierarchical porous carbon, hollow carbon nanospheres, N-doped porous carbon nanosheets, sulfur-doped carbon, and nanowires have been proposed as anode materials for SIBs due to “poor cycling stability” and “low and initial subsequent Coulombi efficiencies" (Li et al., 2017). While anodes utilizing hard carbons are heavy in research and vary in methodology, a commercial carbon molecular sieve, engineered through Zhang et al., achieved a relatively successful construction of a hard carbon-based anode. Through permitting Na-ion insertion within “abundant ultra-small pores,” they achieved a high reversible capacity of 284 mAh g^{-1} at a current density of 100 mA g^{-1} (Zhang et al., 2016).

II. Methodology

Within this paper, we will explore various types of electrode materials and evaluate the feasibility and efficacy of its implementation within the context of sodium-ion grid-scale energy storage systems. As mentioned by Pan et al., it's important to consider factors such as "energy density, specific capacity, discharge performance, power output, response time, cycle life, safety, and cost" (Pan et al., 2013). However, certain factors are more important than others, due to the nature of grid-scale level batteries. Factors such as energy density may be of less concern due to the sedentary usage of the technology. Factors such as safety and response time may be more important due to the possible residential geography of these storage systems. In a perfect world, one would be able to analyze various electrode materials to determine the optimal sodium-ion battery for grid scale technologies. However, as certain processes and statistics are not known, this paper seeks to evaluate electrode materials best within the scope of grid-scale level energy storage systems, providing a helpful resource for energy system designers to understand promising materials for future systems. This paper will also implement a grading score to prioritize and deprioritize certain electrode materials, thus giving a quantitative estimation on how apt an electrode metal is for grid-scale level implementation.

This paper will create a graded ranking set comparing a total of ten electrodes, consisting of seven cathode and three anodes. The seven cathodes include layered oxides {O3, O'3, P3 - Na_xCoO_2, P2 - Na_xCoO_2, $NaCrO_2$, $NaVO_2$}, Prussian Blue and Analogues{R-$Na_{1.92}Fe[Fe(CN)_6]$, $Na_2Mn^{II}[Mn^{II}(CN)_6]$}, and a phosphate {$NaFePO_4$} cathode. The three anodes include a graphitic {Expanded Graphite}, a non-graphitic {Carbon Molecular Sieve [CMS]}, and an alloy {Sn-polyacrylate [Sn-PAA]} anode.

We will rank and organize ten total electrode materials based on their reversible capacity, limiting-material abundance, cycle life and stability, and energy density. Within the larger scope of grid-scale level energy electrical systems, optimizing for safety and overall kWh/$ is key. Factors such as reversible capacity, energy density, cycle life, and material abundance are the same factors used when computing overall kWh/$. Due to the current-day development status of certain electrodes, full information regarding the manufacturing process, reactant costs, and other associated statistics are unavailable. Therefore, this paper will regard these cost-associated factors instead, giving future researchers more specific analysis to base their work off. Within grid-scale level batteries, safety is a key concern with battery technologies. Molten sodium batteries, such as Na-S or Na-O_2, operate at high temperatures (approximately 100°C+) causing safety concerns. As the state of electrode-research does not always include data or information related to safety, this paper will analyze cyclic trends of batteries in regards to safety.

2.1 Weighted-Ranking System

Due to the current nature of electrode research, much information concerning the economic and technological feasibility of certain materials comes within both quantitative and qualitative research. In order to best compare and contrast electrode materials, this paper will utilize a weight-ranking system to evaluate and present results. Within each of the factors (reversible capacity, material abundance, cycle life/stability, energy density), this paper will rank each cathode from 1st to 7th and each anode from 1st to 3rd. Then, each ranking will be multiplied by a weight and summed, resulting in a weighted-ranking score of which we can utilize to assess favorable electrode materials. Lower values will indicate a material as more preferable.

As demonstrated through Table 1 and Table 2, all categories are weighted close to evenly–with the exception of reversible capacity and energy density. Within the scope of grid-scale level batteries, energy density is of less importance due to the lack of batteries' movement. In addition, reversible capacity is noted with more importance as it is a base measurement best demonstrating the technological advancement of the electrode. Thus, this weighted-ranking system will apply a 30% weight to reversible capacity and only a 20% weight to energy density.

Table 1

Weights for Cathode Material Ranking

Material	Reversible Capacity	Energy Density	Cycling Ability	Material Abundance	Total
O3, O'3, P3 - Na_xCoO_2	30%	20%	25%	25%	100%
P2 - Na_xCoO_2	30%	20%	25%	25%	100%
$NaCrO_2$	30%	20%	25%	25%	100%
$NaVO_2$	30%	20%	25%	25%	100%
R-$Na_{1.92}Fe[Fe(CN)_6]$	30%	20%	25%	25%	100%
$Na_2Mn^{II}[Mn^{II}(CN)_6]$	30%	20%	25%	25%	100%
$NaFePO_4$	30%	20%	25%	25%	100%

Table 2

Weights for Anode Material Ranking

Material	Reversible Capacity	Current Density	Cycling Ability	Material Abundance	Total
Expanded Graphite	30%	20%	25%	25%	100%
CMS	30%	20%	25%	25%	100%
Sn-PAA	30%	20%	25%	25%	100%

2.1.1 Reversible Capacity Ranking

Ranking electrodes by reversible capacity is fairly simple, as little calculations are needed. For O3, O'3, P3 - Na_xCoO_2 and P2 - Na_xCoO_2 cathodes from Shacklette et al., the authors provide energy density only (Shacklette et al., 1988). In order to determine reversible capacity for O3, O'3, P3 - Na_xCoO_2 cathodes, this paper takes the charged voltage value (V) and utilizes it within this equation:

$$Reversible\ Capacity_{\blacksquare}\left(\frac{mAh}{g}\right) = \frac{Energy\ Density\ \left(\frac{Wh}{Kg}\right)}{Voltage\ (V)}$$

In this For all other electrodes, reversible capacity is given. Thus, electrodes are ranked from highest reversible capacity to lowest reversible capacity.

2.1.2 Energy Density

Just as reversible capacity is ranked from highest to least, energy density is ranked from highest to least in Wh/kg. For cathodes whose energy density is not given, this formula is used to compute energy density in Wh/kg:

$$Energy\ Density\ \left(\frac{Wh}{Kg}\right) = Reversible\ Capacity_{\blacksquare}\left(\frac{mAh}{g}\right) * Voltage(V)$$

Within anode material literature, authors provide current density in the form of mA/g. For anodes, higher ranking anode materials will have a higher current density than lower ranking anode materials.

2.1.3 Cycling Ability

As per judging cycling ability, ranking electrode materials becomes more complicated. Due to the variation in terms of cycle numbers conducted by each study, ranking was optimized to ensure a higher-ranked electrode had higher capacity retention throughout all cycle numbers than a lower-ranked electrode material.

2.1.4 Material Abundance

This category ranks the limiting element, the element of lowest crustal abundance, within an electrode material by the element's crustal abundance within Earth. Higher ranking electrode materials will have higher crustal abundance of its limiting element than a lower ranking electrode.

2.2 Data

Table 3

Cathode Material Data Table

Material	Reversible Capacity (mAh/g)	Energy Density (Wh/kg)	Cycling Number	Cycle Retention (%)	Material Abundance (PPM)
O3, O'3, P3 - Na_xCoO_2 (Shacklette et al., 1988)	85.7	300	340	50	[Co] 26.6 (Cobalt, 2022)
P2 - Na_xCoO_2 (Shacklette et al., 1988)	77.1	270	1000	50	[Co] 26.6 (Cobalt, 2022)
$NaCrO_2$ (Komba et al., 2021)	120	360	1000	90	[Cr] 135 (Chromium, 2022)
$NaVO_2$ (Shiiba et al., 2013)	173	N/A	N/A	N/A	[V] 138 (Vanadium, 2022)
R-$Na_{1.92}Fe[Fe(CN)_6]$ (Wang et al., 2015)	160	490	750	80	[C] 200 (Carbon, 2022)
$Na_2Mn^{II}[Mn^{II}(CN)_6]$ (Lee et al., 2014)	209	554	100	75	[C] 200 (Carbon, 2022)
$NaFePO_4$ (Liu et al., 2014)	145	168.1	6399	89	[P] 567 (Phosphorus, 2022)

Table 4

Weights for Anode Material Ranking

Material	Reversible Capacity (mAh/g)	Current Density (mA/g)	Cycling Number	Cycle Retention (%)	Material Abundance (PPM)
Expanded Graphite	184	100	2000	73.92	[C] 200 (Carbon, 2022)
CMS	284	100	180	93.3	[C] 200 (Carbon, 2022)
Sn-PAA	500	50	20	100	[Sn] 1.7 (Tin, 2022)

III. Results

Table 5

Cathode Material Ranking

Material	Reversible Capacity	Energy Density	Cycling Ability	Material Abundance	Weighted Ranking
O3, O'3, P3 - Na_xCoO_2	6	4	5	7	5.6
P2 - Na_xCoO_2	7	5	4	7	5.85
$NaCrO_2$	5	3	2	5	3.85
$NaVO_2$	2	7	7	4	4.75
R-$Na_{1.92}Fe[Fe(CN)_6]$	3	2	3	2	2.55
$Na_2Mn^{II}[Mn^{II}(CN)_6]$	1	1	6	2	2.5
$NaFePO_4$	4	6	1	1	2.9

Table 6
Anode Material Ranking

Material	Reversible Capacity	Current Density	Cycling Ability	Material Abundance	Weighted Ranking
Expanded Graphite	3	1	1	1	1.6
CMS	2	1	2	1	1.55
Sn-PAA	1	3	3	3	2.4

3.1 Results of Cathode Material Ranking

Ranked from most to least optimal cathode materials come $Na_2Mn^{II}[Mn^{II}(CN)_6]$, R-$Na_{1.92}Fe[Fe(CN)_6]$, $NaFePO_4$, $NaCrO_2$, $NaVO_2$, O3/O'3/P3 - Na_xCoO_2, then P2 - Na_xCoO_2. Although the specific values of each ranking have greater cause to be disputed, the overall ranking of these electrode materials appears justified. The two highest ranking electrode materials, $Na_2Mn^{II}[Mn^{II}(CN)_6]$ and R-$Na_{1.92}Fe[Fe(CN)_6]$, are both Prussian Blue Analogue materials. Both these materials have high energy density and reversible capacity, in addition to utilizing materials of high abundance. In fact, CATL, one of China's leading battery research organizations, utilizes PBAs in their commercial sodium-ion batteries, potentially due to the same reasons as reviewed in this paper (CATL Unveils, 2021). The worst performing cathode materials include both layered oxides including cobalt. As noted by Yabuuchi et al., cobalt is nearly as scarce as lithium, hence these electrode materials would never solve the material abundance issue which triggered additional interest in sodium-ion batteries. Coming just before the two cobalt layered oxides is $NaVO_2$. This layered oxide had promising reversible capacity, however it lacked cycling ability and stability due to the "large voltage variation during cycling and the oxygen sensitivity of the material" (Shiiba et al., 2013).

3.2 Results of Anode Material Ranking

Ranked from most to least optimal anode materials come Carbon Molecular Sieve (CMS), Expanded Graphite (EG), then Sn-PAA. Both CMS and the EG are carbonaceous materials, with CMS being a hard-carbon and EG being a graphitic material. As both materials are carbonaceous, the limiting material is carbon, which exists at 200 ppm, plentiful for battery production (Carbon, 2022). CMS is cited to perform so well due to the "abundant ultra-small (0.3-05 nm) pores that only allow the insertion of Na ions while rejecting the electrolyte," allowing for a high-performance anode (Zhang et al., 2016). Expanded graphite, on the other hand, provides a competitive reversible capacity in addition to a superior cycle life, with 73.92% retained after 2000 cycles. Due to the large gap between cycle life, one can dispute whether EG or CMS is a superior cathode. Outside of these two, Sn-PAA well-deserved to be ranked worst out of all anodes. Although this anode has nearly double the reversible capacity as CMS, the scarcity of Sn is less than that of Li.

IV. Conclusion

This study reviewed, considered, and compared various electrode materials concerning grid-scale sodium-ion batteries. After reviewing the current and future state of the energy grid in respect to global emissions and climate change, this paper considered the necessities and requirements for successful and cost-effective grid-scale sodium-ion batteries. This study reviewed cathode materials, such as layered oxides, Prussian blue and analogues, and phosphates in addition to anode materials consisting of carbonaceous materials and alloys. Through a proposed weighted-ranking system on the basis of reversible capacity, energy density, cycling ability, and material abundance of various electrode materials, this paper recommends $Na_2Mn^{II}[Mn^{II}(CN)_6]$ and R-$Na_{1.92}Fe[Fe(CN)_6]$ cathode materials. Through the same system, this paper recommends Carbon Molecular Sieves as a preferable anode material based on the same attributes. This paper seeks to provide ample information for researchers in the space of future electrode materials for SIBs in the context of future grid-scale level batteries. This paper also seeks to provide a valid process to compare and rank various electrode materials, in hopes of aiding in determining specific areas of research in electrode material development. Successful usage of this study would hopefully result in rapid research and development of grid-scale batteries of alternative materials, leading to accelerated adoption of these systems. Correlating with increased usage of these storage systems, renewable energy systems, including those that variably produce energy, could be adopted and used within the energy system, advancing our society to a sustainable and carbon-neutral system.

Bibliography

Carbon - Element information, properties and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/6/carbon

CATL Unveils Its Latest Breakthrough Technology by Releasing Its First Generation of Sodium-ion Batteries [Press release]. (2021, July 29). https://www.catl.com/en/news/665.html

Chen, T., Jin, Y., Lv, H., Yang, A., Liu, M., Chen, B., Xie, Y., & Chen, Q. (2020). Applications of lithium-ion batteries in grid-scale energy storage systems. *Transactions of Tianjin University*, *26*(3), 208-217. https://doi.org/10.1007/s12209-020-00236-w

Chromium - Element information, properties, and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/24/chromium

Cobalt - Element information, properties and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/27/cobalt

Delmas, C., Braconnier, J., Fouassier, C., & Hagenmuller, P. (1981). Electrochemical intercalation of sodium in naxcoo2 bronzes. *Solid State Ionics*, *3-4*, 165-169. https://doi.org/10.1016/0167-2738(81)90076-X

Delmas, C., Fouassier, C., & Hagenmuller, P. (1980). Structural classification and properties of the layered oxides. *Physica B+C*, *99*(1-4), 81-85. https://doi.org/10.1016/0378-4363(80)90214-4

Ellis, B. L., & Nazar, L. F. (2012). Sodium and sodium-ion energy storage batteries. *Current Opinion in Solid State and Materials Science*, *16*(4), 168-177. https://doi.org/10.1016/j.cossms.2012.04.002

Fan, X., Liu, B., Liu, J. *et al.* Battery Technologies for Grid-Level Large-Scale Electrical Energy Storage. *Trans. Tianjin Univ.* 26, 92–103 (2020). https://doi.org/10.1007/s12209-019-00231-w

Global electricity demand is growing faster than renewables, driving strong increase in generation from fossil fuels. (2021, july 15). https://www.iea.org/news/global-electricity-demand-is-growing-faster-than-renewables-driving-strong-increase-in-generation-from-fossil-fuels

Gür, T. M. (2018). Review of electrical energy storage technologies, materials and systems: Challenges and prospects for large-scale grid storage. *Energy & Environmental Science*, *11*(10), 2696-2767. https://doi.org/10.1039/C8EE01419A

Hwang, J. Y., Myung, S. T., & Sun, Y. K. (2017). Sodium-ion batteries: Present and future. *Chemical Society Reviews*, *46*(12), 3529-3614. https://doi.org/10.1039/C6CS00776G

IPCC, 2022: Climate Change 2022: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [H.-O. Pörtner, D.C. Roberts, M. Tignor, E.S. Poloczanska, K. Mintenbeck, A. Alegría, M. Craig, S. Langsdorf, S. Löschke, V. Möller, A. Okem, B. Rama (eds.)]. Cambridge University Press. Cambridge University Press, Cambridge, UK and New York, NY, USA,3056 pp., doi:10.1017/9781009325844

Jache, B., & Adelhelm, P. (2014). Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of co-intercalation phenomena. *Angewandte Chemie International Edition*, *53*(38), 10169-10173. https://doi.org/10.1002/anie.201403734

Komaba, S., Takei, C., Nakayama, T., Ogata, A., & Yabuuchi, N. (2010). Electrochemical intercalation activity of layered nacro2 vs. licro2. *Electrochemistry Communications*, *12*(3), 355-358. https://doi.org/10.1016/j.elecom.2009.12.033

Kroposki, B., Johnson, B., Zhang, Y., Gevorgian, V., Denholm, P., Hodge, B.-M., & Hannegan, B. (2017). Achieving a 100% renewable grid: Operating electric power systems with extremely high levels of variable renewable energy. *IEEE Power and Energy Magazine*, *15*(2), 61-73. https://doi.org/10.1109/MPE.2016.2637122

Lee, H.-W., Wang, R. Y., Pasta, M., Woo lee, S., Liu, N., & Cui, Y. (2014). Manganese hexacyanomanganate open framework as a high-capacity positive electrode material for sodium-ion batteries. *Nature Communications*, *5*(1). https://doi.org/10.1038/ncomms6280

Li, L., Zheng, Y., Zhang, S., Yang, J., Shao, Z., & Guo, Z. (2018). Recent progress on sodium ion batteries: Potential high-performance anodes. *Energy & Environmental Science*, *11*(9), 2310-2340. https://doi.org/10.1039/C8EE01023D

Li, Y., Lu, Y., Zhao, C., Hu, Y.-S., Titirici, M.-M., Li, H., Huang, X., & Chen, L. (2017). Recent advances of electrode materials for low-cost sodium-ion batteries towards practical application for grid energy storage. *Energy Storage Materials*, *7*, 130-151. https://doi.org/10.1016/j.ensm.2017.01.002

Liu, Y., Zhang, N., Wang, F., Liu, X., Jiao, L., & Fan, L.-Z. (2018). Approaching the downsizing limit of maricite nafepo₄ toward high-performance cathode for sodium-ion batteries. *Advanced Functional Materials*, *28*(30), 1801917. https://doi.org/10.1002/adfm.201801917

Luo, W., Shen, F., Bommier, C., Zhu, H., Ji, X., & Hu, L. (2016). Na-Ion battery anodes: Materials and electrochemistry. *Accounts of Chemical Research*, *49*(2), 231-240. https://doi.org/10.1021/acs.accounts.5b00482

Manganese - Element information, properties and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/25/manganese

Manthiram, A. (2017). An outlook on lithium ion battery technology. *ACS Central Science*, *3*(10), 1063-1069. https://doi.org/10.1021/acscentsci.7b00288

Nayak, P. K., Yang, L., Brehm, W., & Adelhelm, P. (2017). From lithium-ion to sodium-ion batteries: Advantages, challenges, and surprises. *Angewandte Chemie International Edition*, *57*(1), 102-120. https://doi.org/10.1002/anie.201703772

Pan, H., Hu, Y.-S., & Chen, L. (2013). Room-temperature stationary sodium-ion batteries for large-scale electric energy storage. *Energy & Environmental Science*, *6*(8), 2338. https://doi.org/10.1039/C3EE40847G

Paterakis, N. G., Erdinç, O., & Catalão, J. P.s. (2017). An overview of demand response: Key-elements and international experience. *Renewable and Sustainable Energy Reviews*, *69*, 871-891. https://doi.org/10.1016/j.rser.2016.11.167

Phosphorous - Element information, properties and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/15/phosphorus

Qian, J., Wu, C., Cao, Y., Ma, Z., Huang, Y., Ai, X., & Yang, H. (2018). Prussian blue cathode materials for sodium-ion batteries and other ion batteries. *Advanced Energy Materials*, *8*(17), 1702619. https://doi.org/10.1002/aenm.201702619

R. J. Kerestes, G. F. Reed and A. R. Sparacino, "Economic analysis of grid level energy storage for the application of load leveling," *2012 IEEE Power and Energy Society General Meeting*, 2012, pp. 1-9, doi: 10.1109/PESGM.2012.6345072.

Rudola, A., Rennie, A. J. R., Heap, R., Meysami, S. S., Lowbridge, A., Mazzali, F., Sayers, R., Wright, C. J., & Barker, J. (2021). Commercialisation of high energy density sodium-ion batteries: Faradion's journey and outlook. *Journal of Materials Chemistry a*, *9*(13), 8279-8302. https://doi.org/10.1039/D1TA00376C

Shacklette, L. W., Jow, T. R., & Townsend, L. (1988). Rechargeable electrodes from sodium cobalt bronzes. *Journal of the Electrochemical Society*, *135*(11), 2669-2674. https://doi.org/10.1149/1.2095407

Shiiba, Hiromasa & Hotta, Shota & Nakamura, Tomoaki & Chizawa, Suguru & Nakayama, Masanobu & Yabuuchi, Naoaki & Komaba, Shinichi. (2013). Comparison of Phase Stability in Layered NaCrO2 and LiCrO2 Oxides By First-Principles DFT Calculations.

Shiiba, Hiromasa & Hotta, Shota & Nakamura, Tomoaki & Chizawa, Suguru & Nakayama, Masanobu & Yabuuchi, Naoaki & Komaba, Shinichi. (2013). Comparison of Phase Stability in Layered NaCrO2 and LiCrO2 Oxides By First-Principles DFT Calculations.

Sources of Greenhouse Gas Emissions. (n.d.). US EPA. Retrieved September 2, 2022, from https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions#electricity

Stevens, D. A., & Dahn, J. R. (2000). High capacity anode materials for rechargeable sodium-ion batteries. *Journal of the Electrochemical Society*, *147*(4), 1271. https://doi.org/10.1149/1.1393348

Tin - Element information, properties and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/50/tin

Uddin, M., Romlie, M. F., Abdullah, M. F., Abd halim, S., Abu bakar, A. H., & Chia kwang, T. (2018). A review on peak load shaving strategies. *Renewable and Sustainable Energy Reviews*, *82*, 3323-3332. https://doi.org/10.1016/j.rser.2017.10.056

Vanadium - Element information, properties, and uses | Periodic Table. (n.d.). Royal Society of Chemistry. Retrieved September 2, 2022, from https://www.rsc.org/periodic-table/element/23/vanadium

Wang, L., Song, J., Qiao, R., Wray, L. A., Hossain, M. A., Chuang, Y.-D., Yang, W., Lu, Y., Evans, D., Lee, J.-J., Vail, S., Zhao, X., Nishijima, M., Kakimoto, S., & Goodenough, J. B. (2015).

Rhombohedral prussian white as cathode for rechargeable sodium-ion batteries. *Journal of the American Chemical Society*, *137*(7), 2548-2554. https://doi.org/10.1021/ja510347s

Wen, Y., He, K., Zhu, Y., Han, F., Xu, Y., Matsuda, I., Ishii, Y., Cumings, J., & Wang, C. (2014). Expanded graphite as superior anode for sodium-ion batteries. *Nature Communications*, *5*(1). https://doi.org/10.1038/ncomms5033

Xiao, B., Rojo, T., & Li, X. (2018). Hard carbon as sodium-ion battery anodes: Progress and challenges. *ChemSusChem*, *12*(1), 133-144. https://doi.org/10.1002/cssc.201801879

Yabuuchi, N., Kubota, K., Dahbi, M., & Komaba, S. (2014). Research development on sodium-ion batteries. *Chemical Reviews*, *114*(23), 11636-11682. https://doi.org/10.1021/cr500192f

You, Y., Wu, X.-L., Yin, Y.-X., & Guo, Y.-G. (2014). High-quality prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries. *Energy Environ. Sci.*, *7*(5), 1643-1647. https://doi.org/10.1039/C3EE44004D

Zhang, S.-W., Lv, W., Luo, C., You, C.-H., Zhang, J., Pan, Z.-Z., Kang, F.-Y., & Yang, Q.-H. (2016). Commercial carbon molecular sieves as a high performance anode for sodium-ion batteries. *Energy Storage Materials*, *3*, 18-23. https://doi.org/10.1016/j.ensm.2015.12.004