

Current and future sodium-ion battery research

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Abstract – Adequate storage technologies are needed to allow a transition to renewable energy sources from fossil fuels. Common Lithium-ion batteries are widely used but are limited by availability of materials, price and safety. This review article shows the early stage research on sodium-ion batteries and published discoveries so far. Because of the needed follow up research, techniques are presented as well as ways to evaluate and compare future results.

Keywords – Battery, Sodium-ion, Grid energy storage, Cathode, Anode, Electrolyte, Research, Lithium-ion

1. Introduction

Energy is a key concern for scientists, businesses and policymakers. These concerns will continue to increase due to the decreasing availability of fossil fuels. Additionally, the impending transition from a fossil fuel based economy to one based on renewable energy sources, will result in an ever-increasing need for storage solutions. This need is due to the non-continuous working hours of rising energy sources like solar cells and wind mills. Various storage technologies exist. These can be grouped by field (chemical, biological, electrochemical, electrical, mechanical and thermal) and by purpose (grid storage and transport). The demanded properties are crucial for the development, adaptation and implementation of a successful storage technology.

Batteries convert chemical energy into electrical energy and various models exist: primary batteries can be used only once, whereas secondary batteries allow multiple charges and discharges. Batteries consist of various electrode and electrolyte materials. The discharge process of a half-cell, which involves an active material electrode with a sodium metal counter electrode and requires electrons at the anode material side for the intercalation, is the charge process of a full cell. In the half-cell, ions intercalate into anode during discharge, which is the reason why the half-cell needs to be discharged. For anodes, charging increases voltage, whereas discharging lowers voltage. Lithium-ion batteries gained wide popularity due to their high voltages and energy density, which allows them to be smaller than other battery types such as lead–acid batteries. However, although lithium-ion batteries are widely used (first commercialized in 1991), they are disadvantageous because of their high price, (about 1000\$/kWh compared to lead acid, which is around 300\$/kWh) [1], safety issues [2], and limited natural deposits which can cause a rise in price and a shortage in availability [3]. Cobalt, contained in the cathodes (LiCoO₂), is partly mined in politically unstable countries, which favors a switch to other materials like iron, manganese, titanium or aluminum in the future [1].

Sodium-ion battery research is relatively recent compared to other battery types, but has great potential due to the abundance of sodium. The low price of sodium-precursors,

e.g. (Na₃(CO₃)(HCO₃)•2H₂O), is about \$150/ton, which is 30–40 times cheaper than lithium carbonate [4]. However, the cost of the final sodium used in the battery would be significant higher and the performance of sodium-ion batteries has to increase to leverage the raw material cost.

However, as the demand for lithium continues to increase through car electrification, an increase in price for lithium can be expected. These factors of price (Table 1), abundance, and size make sodium-ion batteries particularly promising for large-scale grid storage applications. Efforts are also being made to develop sodium batteries for electric vehicles [5], but due low intercalations voltages decreasing power density grid storage applications are the most promising in the near future.

Category	Lithium	Sodium
Cation radius (Å)	0.76	1.06
Atomic weight	6.9 g mol ⁻¹	23 g mol ⁻¹
SP E° (vs. Li/Li⁺)	-3.04 V	-2.71 V
Cost, carbonates	3850€/ton	115€/ton
Capacity (mAh g⁻¹), metal	3829	1165
Coordination preference	Octahedral and tetrahedral	Octahedral and prismatic

Table 1. Comparison of properties lithium and sodium; adapted from [4]

Existing grid-storage technologies (Figure 1) have, next to their individual advantages, their drawbacks. Pumped storage hydroelectricity has high capital costs and geographical limitations. Hydrogen storage systems suffer from rather low mass absorption capacities, and hydrogen self-discharge and the requirements of a thermal management system. Supercapacitors have a limited lifespan and a high self-discharge rate. Lead-acid batteries have a relatively low cycle life and battery operational lifetime as well as the toxicity of lead. Flywheels are expensive and incur high standing losses [6].

There exist sodium batteries which work well at room temperature, whereas others need a high temperature environment. Although Na/S and Na/NiCl₂ batteries offer useful energy densities, they have poor power densities.

However, because liquidized sodium functions only at high temperatures (300-250°), the operation and maintenance of these batteries is more difficult, resulting in higher kWh costs (about 380-460€) [4]. Although there has been an increase in the number of publications regarding sodium batteries at high temperatures, with the ambition to reduce the required temperature to 100-150 °C, [7] this review focuses on sodium-ion batteries capable of working at room temperature.

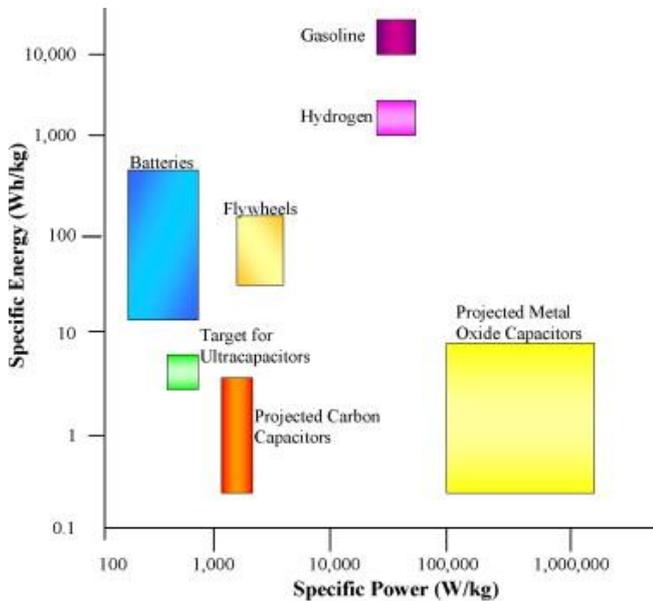


Figure 1. Comparison of specific power and energy storage potential of each storage technology [6]

2. Current research

Since research is still in its early stages, many findings are not patented and published yet. However, recent publications give an overview of current sodium research.

2.1. Dual intercalation systems

The market dominating lithium-ion battery consists of LiCoO_2 as the cathode and graphite as the anode. In the initial charging, the graphite gets lithiated forming LiC_6 as an intercalation product in the anode. During the discharge the Lithium intercalated in the anode donates an electron and moves through the electrolyte back to the cathode where the starting material LiCoO_2 is formed. From here the battery can be charged again allowing another discharge. This cycle can be repeated as long the reaction stays reversible (battery cycle life) [8]. The general scheme for dual intercalation systems can be seen in figure 2.

The intercalation host materials and other battery components contribute the main mass for such a battery system. Hence, the larger size and weight of Na atoms compared to Li atoms does not have such a high impact. However, because of the larger size, intercalation materials for sodium batteries need large-enough channels and interstitial sites (space in array atoms which can be occupied). Furthermore, they need to show high electronic and ionic conductivity [4].

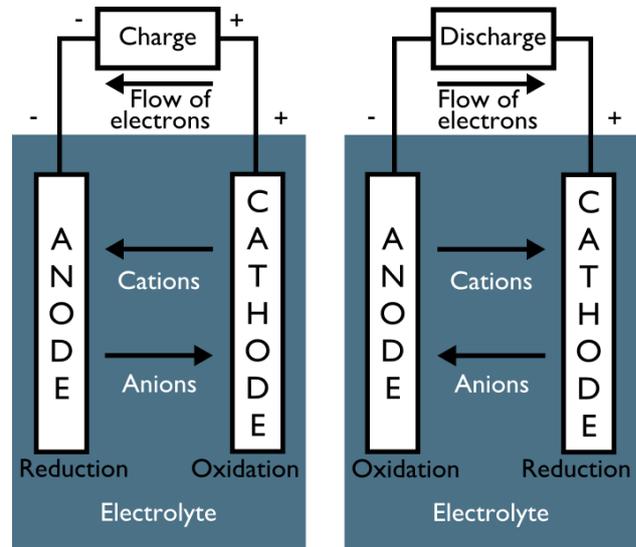


Figure 2. Chargeable cell / battery diagram convention

Following the schemata of existing lithium-ion batteries, an intercalation sodium battery could consist of an anode made of a high-capacity, dense Na-metal alloy (e.g. Na metal, Na_4Sn or Na_xC) and a high-capacity cathode. Because sodium metal has, at 97.72 °C, a lower melting point than lithium (180.5 °C), room temperature poses a risk for Na metal electrodes. Following this, true cycled ion systems are needed that avoid the highly reactive Na metal (Figure 3). However, because of the early research state of sodium batteries, most electrodes and materials are tested with Na metal half cells [4]. Next to other published research [9] some recent electrode candidates are shown below.

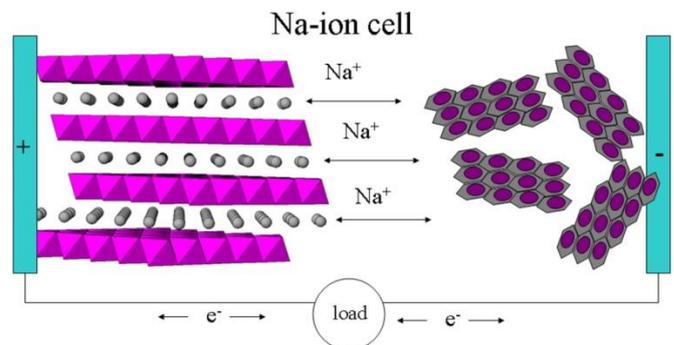


Figure 3. Basic illustrated dual intercalation mechanism of a sodium-ion battery [10]

2.1.1. Cathodes

2.1.1.1. NaFeO_2

Following the common use of lithium-transition metal-oxide as cathodes for lithium-ion batteries, a derivative of that structure where sodium replaced lithium was prepared. These NaFeO_2 cathodes showed excellent reversibility for a cut-off voltage of 3.4, whereas this wasn't the case for higher voltages (Figure 4). Irreversible structural changes could be observed at 4.0 V, which even increased for 4.5 V, explaining the loss in reversibility [11].

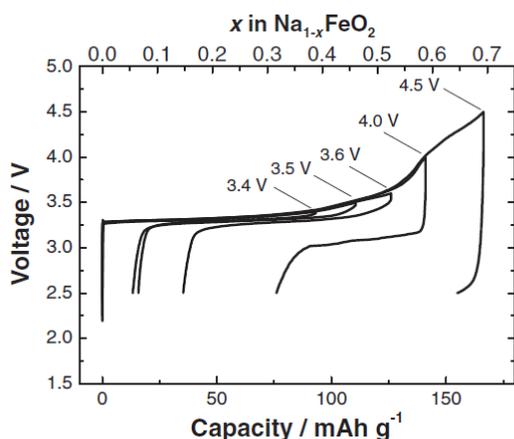


Figure 4. Initial charge/discharge curves of Na/NaFeO₂ cells with different cut-off voltage at a rate of 12mA g⁻¹ [11]

2.1.1.2. Na(Ni_{1/3}Fe_{1/3}Mn_{1/3})O₂

Na(Ni_{1/3}Fe_{1/3}Mn_{1/3})O₂ cathodes were tested in systems with carbon anodes and an organic electrolytes. Underlying a charge / discharge rate of 0.5 C-rate (charged and discharged in 2h each) between 1.5 and 4.1 V, 150 cycles were reached with a faradaic efficiency of 99% whereas the capacity dropped from 120 mAh/g to 80 mAh/g (Figure 5) [10].

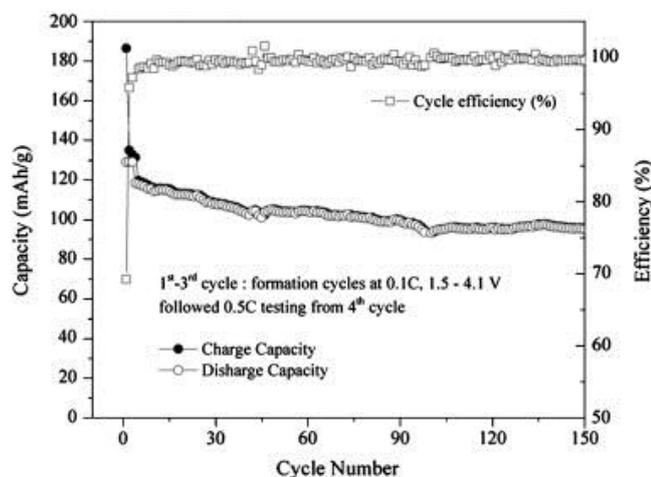


Figure 5. Na-ion Na_xC/Na_{1-y}(Ni_{1/3}Fe_{1/3}Mn_{1/3})O₂ cell long term cycling (capacity versus cycle number) and faradaic efficiency at a charge-discharge 0.5C rate (75 mA g⁻¹) between 1.5 and 4.1 V [10]

At this stage, the corresponding energy density for the active materials with 273 Wh kg⁻¹ is too low for an average cell voltage of 3.0 V [4] compared to the energy density of lithium-ion batteries with theoretical 400-500Wh kg⁻¹ [12] and around 180 Wh kg⁻¹ for a battery on a cell level [13].

2.1.1.3. Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_δ

This cathode material is one example of the tested layered oxides Na_xLi_yNi_{0.25}Mn_{0.75}O_δ (0.7 ≤ x ≤ 1.2; 0 < y ≤ 0.5) which were found to have characteristics of high-rate reversible intercalations of Na. Lithium was used to stabilize the transition metal layer in a charge-ordering state between Ni(II) and Mn(IV), as it was observed before in other systems (e.g. Li_{1.2}Ni_{0.2}Mn_{0.6}O₂). The oxide cathode showed a modest performance and stability for a reversible Na intercalation [14]. Unfortunately, only very few cycles (up to 5) were run and no long-term behavior was determined. Because of the

use of lithium, advantages to standard lithium-ion batteries are needed to support the use of lithium containing oxide layer cathodes.

2.1.2. Anodes

2.1.2.1. Carbon-based

Graphite is the most commonly used anode for lithium-ion batteries. However, as early as 1988 papers were published demonstrating that sodium-graphite anodes show only very poor performance. [15] Because of this other carbon containing materials were tested, where hard-carbons (carbon materials synthesized at round 1000 °C) and glassy carbon (has a fullerene-related microstructure) showed better sodium intercalation properties. At low voltages, the nanopores get filled, whereas Na intercalates at higher temperatures into the nanocavities [4].

2.1.2.2. α-MoO₃

The first research on alpha-MoO₃ has only recently been published. The observed electrode performance was comparable to carbon and Na₃V₂(PO₄)₃ cathodes. 500 cycles could be achieved with a 0.2 C-rate. The efficiency stayed nearly constant close to 100% whereas the capacity dropped from 210 to 110 mAh g⁻¹. The storage performance of the MoO₃ was comparable to anode materials like carbon. However, the theoretical potential sodium uptake is with round 0.793 V less than half than the one of lithium. However, the obtained voltage profile is promising. Combined with a Na₃V₂(PO₄)₃ cathode a 1.4 V sodium-ion battery was obtained. Further studies to evaluate the details of sodiation and desodiation of this anode are in progress [16].

2.1.3. Electrolytes

2.1.3.1. Non-aqueous

For the previous mentioned cathodes and anodes, non-aqueous electrolytes are used to insure a flow of ions, as is the case for lithium-ion batteries. The most commonly used electrolytes are NaPF₆ and NaClO₄ as salts in propylene carbonate (PC). To ensure proper functioning, a solid electrolyte interphase (SEI) has to be formed which insulates yet allows enough ions to pass through. PC causes inefficiencies due to produced impurities with Na electrodes. More research on additives and alternative solvents (like fluoroethylenecarbonate) is needed to develop optimally tailored electrolytes [4].

2.1.3.2. Aqueous

In contrast to the aforementioned electrolytes, a recent alternative approach is to take aqueous electrolytes based on salt water. An aqueous hybrid ion (AHI) battery was developed by Jay Whitacre (Professor at Carnegie Mellon) in 2008. Aquion Energy, a company dedicated to this technology, uses activated carbon as an anode and Manganese Oxide (MnO₂) as a cathode. These materials are already used in common alkaline batteries and some Lithium-ion batteries. Furthermore they use synthetic cotton separators between the cathode and anode [17]. The first prototypes were shipped in late 2012 and they plan to build the first factory in the next 3.5 years [18]. Other research groups are focusing on aqueous electrolytes as well [19].

3. Future research

Since sodium-ion battery research is still in its early stages, further research is needed. In the following section helpful techniques are summarized, as well as methods for comparison and more efficient research strategies.

3.1. Synthesis

The synthesis for various electrode materials differs in both the materials and procedures used. Experimental sections are published to summarize the used protocols [10]. Further resources containing detailed instructions are often available online. Unfortunately, the access to commercial research is highly restricted but can later be viewed in released patents.

3.2. Characterization

3.2.1. X-ray crystallography

X-Ray crystallography (XRD) is one of the main techniques to characterize new materials [20]. XRD can be also used to determine if there are unreacted phases on the product [21].

3.2.2. Energy-dispersive X-ray spectroscopy (EDS)

The Energy-dispersive X-ray spectroscopy (EDS) is used in the characterization of electrodes by determining the elements present [21].

3.2.3. Electron microscopy

The scanning electron microscope (SEM) [22] and Transmission electron microscopes (TEM) [23] can be used to characterize material samples. With these techniques one can find the (average) diameters of nanoparticles (NPs) (Figure 8).

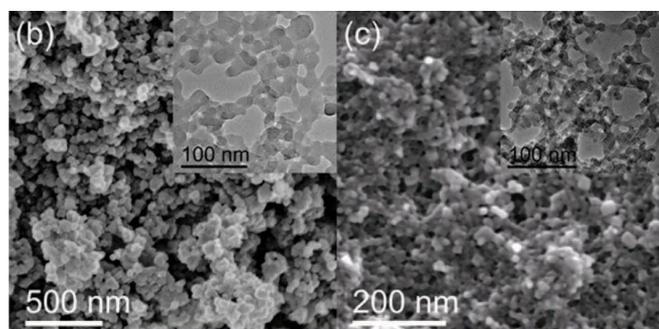


Figure 6. TEM images of NaFeHCF and KFeHCF nanoparticles [21]

3.3. Preparation and testing of coin cells

Text and video manuals for LiCoO₂ CR2032 coin cells (CR2032 are available at the MTI Corporation) were published by and for the scientific community [24]. This information can be transferred to the assembly of sodium-ion coin cells. Different coin cell sizes, counter electrodes (not Li or Na respectively), binders and electrolytes can be used to fit different purposes. For the assembly a glove box with argon is needed to create an inert atmosphere (especially no moisture). Commercial testing stations (Figure 9) exist in various functions and sizes.



Figure 7. Loading a lithium coin cell for testing on an Arbin battery cycler at the Lawrence Berkeley National Laboratory [25]

Before the electrodes can be evaluated with X-ray crystallography, they are extracted from the coin cells, washed with a solvent (dimethylcarbonate, DMC) and dried in a He glove-box [14].

3.4. Evaluation

Once the battery components are characterized and their performance is determined, they are evaluated against the available data of other products. For example diagrams based on operating voltage, capacity and energy density are available to compare results (Figure 10).

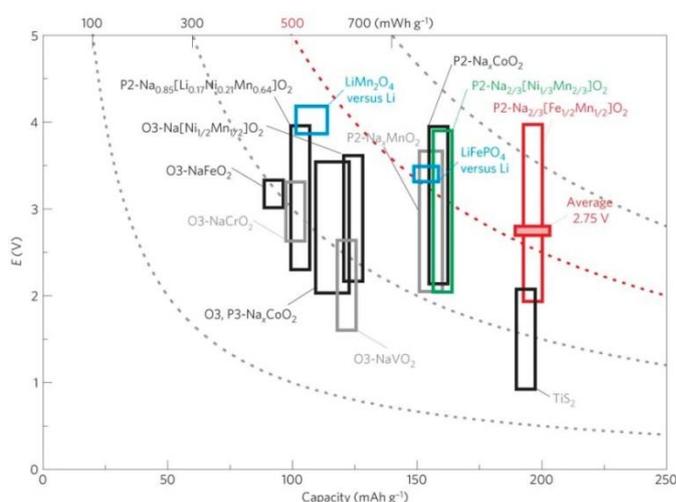


Figure 8. A comparison of reversible capacity and operating voltage ranges of the layered sodium insertion materials [26]

After evaluating the individual parts of a battery, tested batteries can be drawn in Ragone charts to show their energy density vs. power density (depended on the C-rate) compared to other batteries (Figure 11).

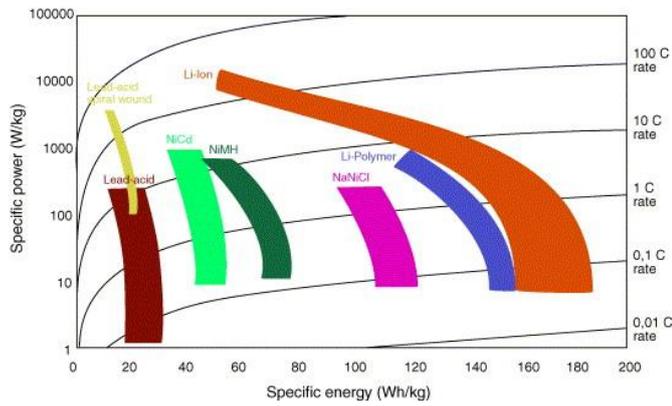


Figure 9. Ragone chart with different battery types [27]

However, these charts display only the performance of the batteries. Further details such as price and operating temperature are crucial for a successful implementation. For car batteries, guidelines (FreedomCAR) were developed by the US Department of Energy which state a 15-year lifetime with 5000 cycles. A comparison of actual lithium-ion batteries with the guidelines can be seen in chart below (Figure 12). However, there are more characteristics to consider, like safety.

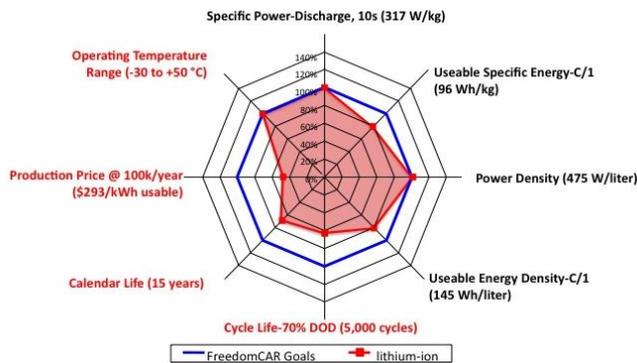


Figure 10. "Spider chart" to compare actual performance of lithium-ion batteries with the goals of the FreedomCAR guidelines [1]

3.5. Materials Project

The Materials Project was founded in 2010 by Prof. Gerbrand Ceder (Professor at MIT) and Dr. Kristin Persson (Research Chemist Scientist at the Lawrence Berkeley National Laboratory). Computation is used to predict characteristics of new materials, before they have been synthesized. The underlying data-mining techniques allow calculations on larger scales. [28]. The project intends to find new materials for Li-ion ion batteries. So far the accessible database contains 405 lithium intercalation compounds and 15,175 conversion battery compounds, and the database is continuously growing. One of its aims is to shorten the time needed to move a new material from the lab to the market, which is currently 18 years on average [29]. Something similar for sodium-ion batteries also has high potential because of the early research state of the discovery of suitable materials.

3.6. Transformation of discovery into business

It can be a tedious process to get from the idea to a working product which can be produced in a large scale and generates profit. Failures can happen throughout the entire process. Jay Whitacre, founder of Aquion Energy, highly

suggests to focus completely on each "proof step," to define clearly pass/fail-criteria and to only do the necessary work to prove each step [18]. After each proof step extra funding might be necessary before the manufacturing can begin (Figure 13).

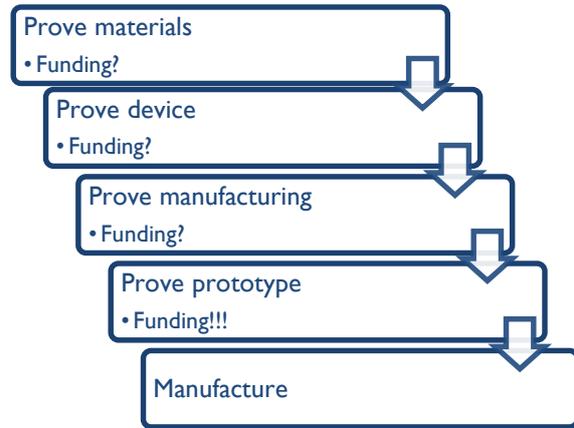


Figure 11. Proof steps from starting with materials until manufacturing, adapted from [18]

3.7. Outlook

To increase the energy density there are three optimizations available: enlarge the capacity, increase the voltage or decrease the amount of inactive material [1]. To bring a battery to the market, costs have to be evaluated for the selected materials, their required purity, the manufacturability performance in terms of costs per kWh, reliability, and safety [18]. Optimization is the key to developing further technologies, alongside advanced and cross-border disciplines and countrywide state-of-the-art-research. It will therefore be helpful to use the knowledge attained in related battery research, such as that done on lithium-ion batteries. One approach in this direction is the concept of sodium-air batteries.

3.7.1. Sodium-air

Zinc-batteries and fuel cells (oxidizing zinc with oxygen from the air) have low prices and a high energy density. A potential next step in the development of the air-battery would be lithium-air batteries, which would deliver eight times more energy compared to the pendant with zinc [13]. However, safety issues remain and so far only low power outputs have been obtained [12]. Therefore, leading representatives and researchers in the automotive industry doubt an implementation in near future, if ever [30].

A sodium-air battery would theoretically deliver four times the energy compared to a traditional lithium battery of the same weight. The running temperature higher than 100° C (above melting temperature of sodium) results in a resistance against water (exceeding the vaporization temperature). In one study, two electrolyte systems (ionic and polymer) were used for three different cells which differed in one electrode (planar-carbon electrode, microporous-layer-carbon electrode and cobalt oxide electrode). The cobalt oxide electrode showed the lowest performance and the sodium aluminum cell ran for 300 cycles with a faradaic capacity of 80% (one is aiming for 99.9%). For low currents the cells weren't charged at all, a behavior which cannot yet be explained. Only a few tests were run and further testing is necessary to evaluate long-term behavior [12].

4. Conclusion

In this review, current research and findings on sodium batteries were described as well as techniques and methods for future research were summarized. Existing electrodes and electrolytes are in an early stage of development and more intense research is needed to be able to mass produce sodium-ion batteries. A continuous evaluation of advantages and disadvantages compared to other existing technologies allows sound research decisions. The insights gained through lithium-ion battery research are useful for future research on the counterpart with sodium. This is also valid for exploring new approaches like sodium-air batteries. Interdisciplinary and broad collaborations between experts in the field, together with a coordinated exchange of information, will be highly beneficial for upcoming research.

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