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Difference in First Cycle Irreversible Loss between Li-ion batteries with Graphite as Anode and Na-ion Batteries with Hard Carbon as Anode

Bachelor's thesis in Chemistry (KJ2900)

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Abstract

The purpose of this paper is to review the effects of first cycle irreversible loss of capacity in lithium-ion batteries (LIBs) containing a graphite anode and sodium-ion batteries (SIBs) containing a hard carbon anode. Battery structure, graphite's and hard carbon's structure and properties, solid electrolyte interphase (SEI) and first cycle loss will be discussed, as well as alternative anode materials briefly. The main discussion in this paper is the cause of first cycle irreversible loss. This is caused by the formation of a SEI layer on the anode material (in the case of LIBs and SIBs). The SEI is necessary for the battery to function properly over time, meaning in order to reduce first cycle irreversible loss, an optimization of the SEI is necessary. In addition to this, the energy density and the price of LIBs and SIBs will be considered, as well as environmental friendliness. In areas where price and/or environmental friendliness is more important than energy density, SIBs could prove to be a substitute for LIBs, in a future where LIBs and SIBs coexist.

Sammendrag

Hensikten med denne artikkelen er å gjennomgå effekten av første syklus irreversibelt tap av kapasitet i litium-ion batterier (LIBs) som inneholder en grafittanode og natrium-ion batterier (SIBs) som inneholder en anode av hard karbon. Batteristruktur, grafitt og hardkarbons struktur og egenskaper, solid elektrolytt interfase (SEI) og førstesyklustap vil bli diskutert, samt alternative anodematerialer kort. Hovedfokuset i denne artikkelen er å se på årsaken til irreversibelt tap i første syklus. Dette er hovedsakelig grunnet dannelsen av et SEI-lag på anodematerialet (i tilfellet for LIBs og SIBs). SEI er nødvendig for at batteriet skal fungere skikkelig over tid, noe som betyr at for å redusere første syklus irreversibelt tap, er en optimalisering av SEI nødvendig. I tillegg til dette vil energitettheten og prisen på LIB og SIB bli vurdert, samt miljøvennlighet. På bruksområder hvor pris og/eller miljøvennlighet er viktigere enn energitetthet til batteriet, vil SIB-er kunne vise seg å være en erstatning for LIB-er, i en fremtid hvor LIB-er og SIB-er sameksisterer.

1: Introduction

Lithium-ion batteries (LIB) and sodium-ion batteries (SIB) are important energy storage technologies, both for stationary and mobile energy storage, that have significant applications in various fields, including electric vehicles and renewable energy systems to name a few (1). Among the available energy storage technologies at this point in time the LIB has the highest energy density (2). However the LIB is far from perfect and has flaws such as having poor low-temperature performance because of the growth of the solid electrolyte interphase (SEI) (3). The performance of these batteries depends to a reasonable extent on the properties of their anode materials, which play a critical role in storing and releasing charge. Availability and cost is another crucial part when it comes to LIBs vs SIBs (4). That being said, SIBs could take over some of the roles LIBs have in markets where price is more important than energy density.

One important metric that measures the performance of battery anodes is first cycle loss, which refers to the irreversible loss of capacity that occurs during the first charging and discharging cycle of the battery. A good battery should consist of an anode with long cycle life and low irreversible capacity (5). First cycle loss is influenced by various factors, including the anode material properties, the cell design and the operating conditions and can e.g. cause lithium batteries to lose 5-20% capacity in the first cycle (6). Reducing first cycle loss is critical for improving the overall energy density which in return improves the energy efficiency.

The focus of this paper is to investigate the difference in first cycle loss between graphite in LIBs and hard carbon in SIBs. Specifically, aiming to compare the performance of these anode materials and identify the factors that contribute to their first cycle loss.

Understanding the difference in first cycle loss between graphite and hard carbon anodes is important for advancing the development of LIBs and SIBs. This knowledge can inform the design and optimization of anode materials and cell configurations that can minimize first cycle loss and improve the overall performance of these batteries (7). This is especially crucial for SIBs, since LIBs has been extensively researched already and a lot is known for the LIBs. E.g., DOI: 10.1016/j.carbon.2016.04.008, the SEI layer forms preferably at the edge plane where Li ions enter and the conductivity in this direction is much higher. Which is why

graphite is shaped and coated in LIBs (8). These details are incredibly important in developing a more extensive understanding of the SIBs and to find ways to improve them further.

2. Literature review/Theory

2. 1. Battery's structure

Batteries are made up of one or more electrochemical cells, which are devices that convert chemical energy into electrical energy. Each cell consists of two electrodes, an anode (negative electrode) and a cathode (positive electrode), which are separated by an electrolyte. The cathode is typically made either Li or Na transition metal oxides or compounds such as lithium cobalt oxide (LiCoO_2). The transition metal does take up or release an electron as Li or Na leaves or enters the structure. The anode in the LIBs looked at in this paper is made of graphite, and the anode material for the SIBs is hard carbon.

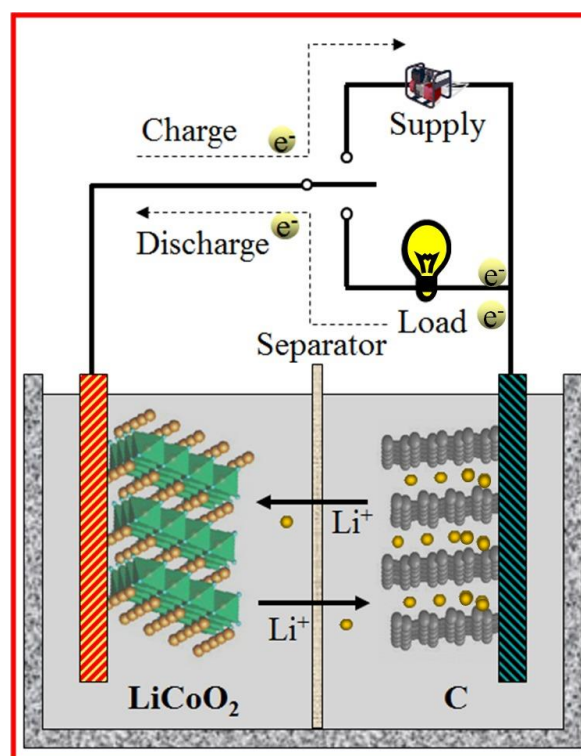


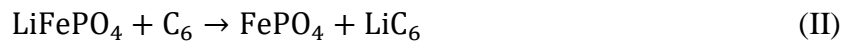
Figure 1: Illustration showing the operation principle and basic components of an example Li-ion cell (9).

During charging, cations (either lithium or sodium, depending on the battery type) are extracted from the cathode and intercalated into the anode. This process is driven by an external electrical current that is applied to the battery. When the cell discharges, electrons are released by the anode and flow through an external circuit to the cathode, where they combine with the intercalated cations and reduce the metal oxide to its original state. The intercalated cations are released from the anode and move through the electrolyte to the cathode, where they recombine with the metal oxide and release energy in the form of an electrical current (9).

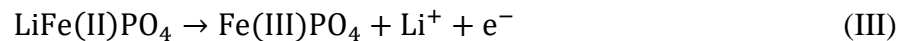
An example charge/discharge cycle of a LIB cell with graphite as anode and LiCoO₂ as cathode would have the following cell reaction during charging:



Having a cathode that can completely empty, like LiFePO₄, makes for a more straight forward reaction during charging:



Where the cathode half-cell reaction would be:



And the anode half-cell reaction would be:



Where the reactions would be reversed during discharge.

2. 2. Lithium battery anodes

There are several types of anode materials that have been developed, researched and used in LIBs, some of which have shown more promising results than others in terms of performance and stability. Silicon (Si) and tin (Sn) anodes are both alloying anodes. Si anodes have a high theoretical specific capacity, in addition to being found in abundance, making it an attractive material for use in LIBs (10). Sn anodes are also attractive because of its high gravimetric capacities, low cost, high safety and so on (11). Unfortunately, both Si and Sn, gives rise to significant volume expansion (approximately 400%) during the reaction that alloys/dealloys the anode with lithium, causing the material to break down over time (12), (13). This causes a loss in electrical contact between neighbouring Si fragments, causing the battery to lose specific capacity, limiting its practical use (14).

Lithium titanate (Li₄Ti₅O₁₂) anodes has a high voltage profile, approximately 1.55V compared to Li-graphite having 0.1V, which makes it a safer alternative to graphite anodes. It also has a long cycle life and fast charging capabilities. It does however have low specific capacity and a relatively high cost, limiting it as a widespread adoption relative to other anodes (2).

Even with good alternatives to the anode material in the LIB, the graphite anode is still the most widely used material due to its high capacity, low cost, lightweight and good cycling stability (15). It is also hard to create stable SEI layers on materials such as Si, Li and Sn, due to their large volume change during cycling (16). Graphite has its own drawbacks as well, one of them being first cycle irreversible capacity loss. First cycle irreversible loss of capacity can be caused by several factors, such as side reactions, structural damage, impurities, etc., but in the case of LIBs with graphite as anode the first cycle loss is mostly caused by surface film growth (17).

2. 3. Sodium battery anodes

SIBs may use metal oxide anodes, alloy anodes, etc., but the hard carbon anodes have some advantages when it comes to its low cost, relatively high capacity and environmental friendliness. Using graphite as the anode material, like for LIBs, has been researched, but unlike lithium, sodium does not form stable intercalation products with the graphite (18). The hard carbon anode is currently seen as the best anode and the anode with best potential in SIBs as of 2023. One of the main reasons why a hard carbon anode is so attractive is the fact that it can be produced a lot cheaper than other anodes that include metals, etc. Hard carbon can be made from organic waste such as corncobs, apple waste and peanut shells (19). Unfortunately it also has its drawbacks, such as that the hard carbon anodes have poor cycling stability and high first cycle loss, which at this point in time is hindering its wider application in SIBs (19). The hard carbon will also have different properties depending on what material it is made from. In addition to this, it also experiences first cycle irreversible loss, like most batteries, because of the side reactions that occur at the electrolyte-anode interface, which then leads to the formation of a SEI layer on the anode surface (20).

2. 4 Anode material properties, structure and composition

2. 4. 1 Graphite anodes (crystal structure and properties)

Carbon naturally occurs in two main forms, diamond and graphite, which differs in its hybridization state being respectively sp^3 (diamond) and sp^2 (graphite). Graphite consists of layers of graphene that are sp^2 hybridized and held together by the weak van der Waals forces of their delocalized electron orbitals. The weak interaction between layers in the graphite facilitates the intercalation of ions, leading to the formation of graphite intercalation

compounds. The graphite layers can stack in three different modes, being hexagonal (AA), Bernal (AB) and rhombohedral (ABC), and with a layer-layer distance of 3.35 Å. The density of graphite is around 2.15-2.25 g/cm³ (21). The fundamental properties of the graphite depends on the stacking mode of the graphite layers, because of the 2p_z orbitals interacts different depending on the stacking. Although the stacking pattern of graphite layers determines its band structures and density of states, which affect its conductivity and electrochemical performance as an anode, the correlation between its crystal structure and physical/electrochemical properties has not received sufficient attention (22). It is also worth noticing the difference in natural graphite and synthetic graphite, both in their properties and how they are processed, since they both can be used as anode material in LIBs. Purified natural graphite exhibits a higher crystalline structure compared to synthetic graphite and is because of this more electrically conductive. Synthetic graphite is being researched to increase its electrochemical properties, but currently natural graphite offers more favourable electrochemical properties, as well as being significantly cheaper, coming in at around 8 USD kg⁻¹, compared to the 13 USD kg⁻¹ for synthetic graphite (as of 2016) (23). The price difference is mostly related to the energy cost during the graphitization process (24). This makes natural graphite the natural choice when it comes to most LIB production, but it is worth mentioning that the EU has classified natural graphite as a critical raw material, and since graphite can be synthesized, it gives synthetic graphite an advantage with increasing demand and lack of availability of natural graphite (25).

2. 4. 2 Hard carbon anodes (crystal structure and properties)

Hard carbon is a type of carbon material that does not become graphitized even when exposed to high temperatures. It is usually produced by pyrolyzing macromolecular polymers. The structure of hard carbon includes curved graphene sheets that cannot be flattened or unfolded which makes it unable to be stacked into graphite (26). The inability of hard carbon to be graphitized can be attributed to the presence of covalent C-O-C bonds and interlayer cross-linking in its precursors (27). As illustrated in figure 2, hard carbon is composed of small graphene sheets, amorphous regions containing defects, and pores. The layer-layer distance in hard carbon is around 3.7-4.0 Å (28). In comparison to graphite, the hard carbon is less organized and contains more defect sites, as well as a larger surface area. The graphitic domains or pseudo-graphite in hard carbon exhibit limited lateral dimension of about 40 Å and restricted stacking of 2-6 layers, ordered over a short range. There are various types of hard carbon such as resin carbon, organic polymer pyrolysis carbon, carbon black, and

biomass carbon. The density of hard carbon is about 1.45-1.55 g/cm³ (21), and its properties may be affected by what type of hard carbon it is and what it's made of off. The sources of hard carbon are abundant, for example, phenolic resin, epoxy resin, poly furfuryl alcohol, covalent organic framework, carbohydrate, cellulose, microbacteria, and peel (20).

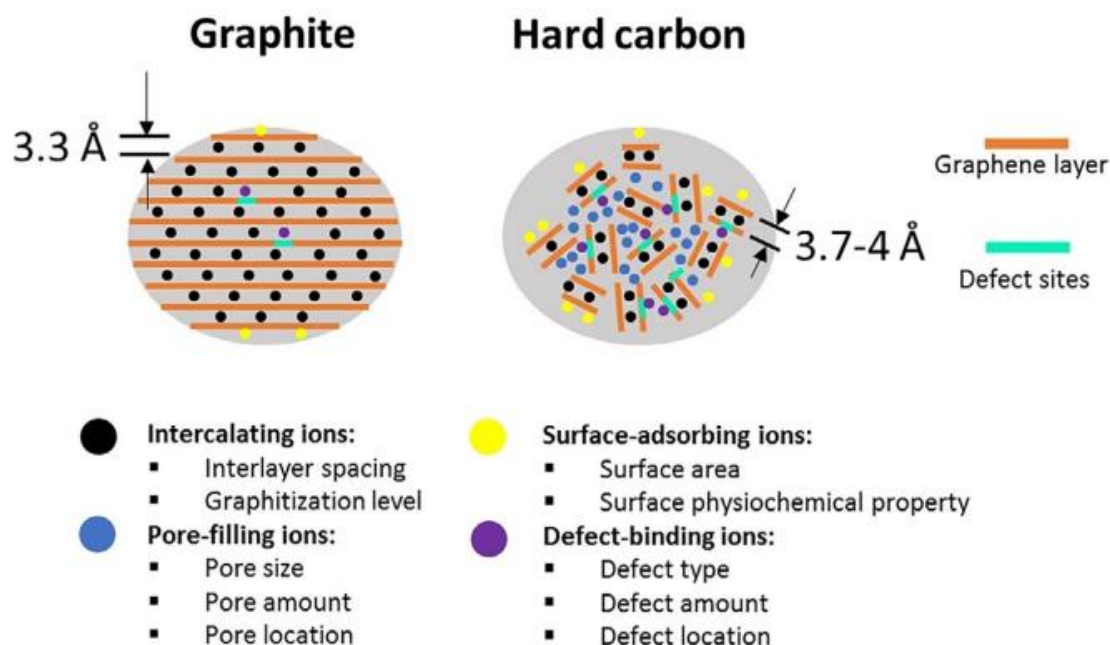


Figure 2: Illustration of the difference between graphite's and hard carbon's ion storage (28).

2. 5. Solid electrolyte interphase (SEI)

The SEI layer that forms during irreversible side reactions are crucial for a battery to work safely over longer periods of time. It consists of solvents and salts that gather on the surface of the anode because of decomposition of electrolyte by either electrochemical or chemical reactions (29). SEI formation happens during the first cycle of the LIBs and SIBs, where the SEI layer forms on the graphite and hard carbon surfaces respectively (8). The SEI layer serves as a protective layer that stabilizes the electrode-electrolyte interface and prevents further reactions between the electrolyte and the electrode. Figure 3 illustrates the initial SEI layer formed on the graphite during the first cycle in a LIB. It is important to note that the SEI's composition is determined by many factors, such as the electrolyte, so the structure of the SEI may vary from the one in figure 3. This protects the electrode from further degradation which would lead cause the battery to malfunction. Additionally, the SEI layer also plays a crucial role in the overall performance and lifetime of the battery by enabling stable and efficient cycling of the battery (30). The SEI layer should be physically strong or

flexible enough to accommodate the volume change (expansion during charging and contraction during discharging) of the anode during the cycling process. The SEI layer should ideally be uniformly distributed over the anodes surface (8).

However, the formation of the SEI layer during the first cycle of charging and discharging of the battery can cause some irreversible capacity loss, which is undesirable. Hence, researchers are working to improve the properties of the SEI layer and minimize its impact on the battery's performance.

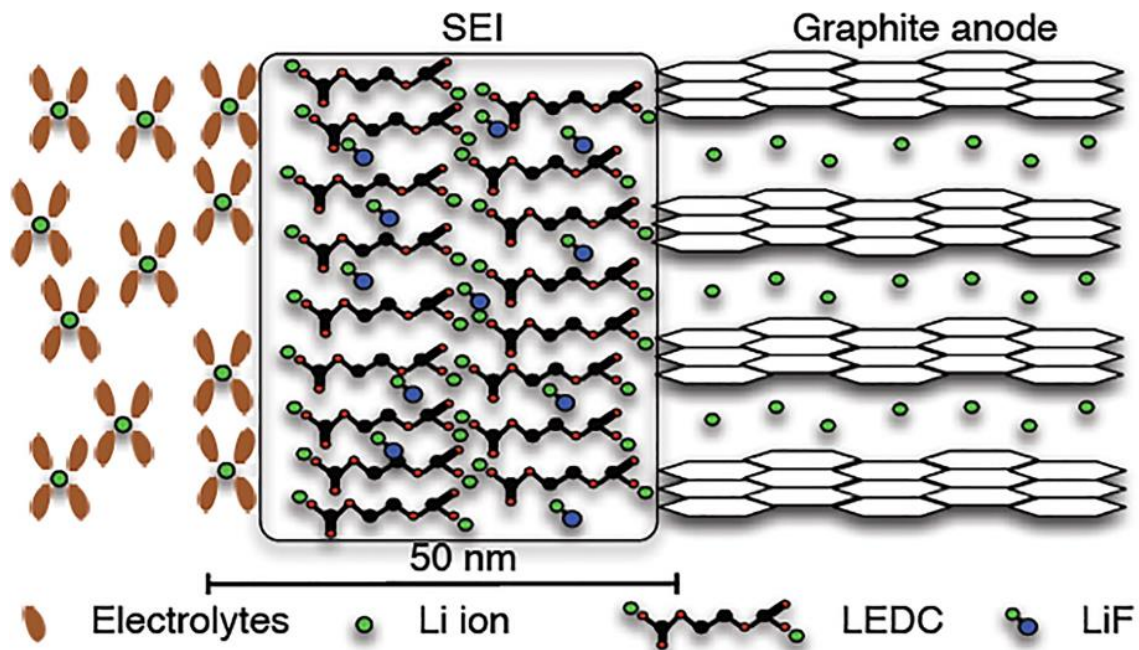


Figure 3: A schematic illustration showing the initial SEI layer formed on the surface of the graphite anode during the first cycle of a LIB (31).

2. 6. First cycle irreversible loss in LIBs and SIBs

First cycle irreversible loss is a term used to describe the battery's loss in charge during the first cycle of charging, caused by irreversible side reactions. In both LIBs and SIBs this process is almost exclusively influenced by the formation of a SEI layer, but first cycle irreversible loss can also be caused by other factors such as changes happening in the structure of either electrode during the first charging cycle. The SEI layer on the anode material's particles that prevents further electrolyte decomposition at the anode (32).

2. 6. 1. First cycle irreversible loss in LIBs

In the case of graphite anodes in LIBs, the first cycle irreversible loss is caused mostly by surface film growth, or the creation of the SEI layer, on the graphite anode. The formation of

the SEI consumes active lithium ions, becoming the main cause of first cycle irreversible capacity loss (16). In addition to SEI formation, it has been found that the irreversible intercalation of lithium ions on the new surface that is formed during the first cycle, specifically in the potential range where lithium ions are intercalated also contributes to first cycle loss (17). Lithiated carbons are unstable in air, so LIBs are always assembled in a discharged state with graphite and lithiated positive materials. At low and very high potentials vs. Li/Li^+ , the electrolyte solution is thermodynamically unstable. Therefore, during the first charge of the cell, the electrolyte solution starts to break down or degrade on the graphite surface, resulting in the formation of the SEI. The SEI layer is a very complicated layer consisting of inorganic components that normally comes from salt degradation products, and organic components that can be either partially or fully reduced forms of the electrolyte solvent (30).

2. 6. 2. First cycle irreversible loss in SIBs

As for the LIBs, the majority of the first cycle irreversible loss comes from the formation of a SEI layer. The SEI layer in hard carbon SIBs is formed on the hard carbon anode material if the Fermi level of the anode material is higher than the lowest unoccupied molecular orbital of the electrolyte (33). As a result, the electrolyte undergoes an automatic decomposition process and forms a solid layer called SEI, which is composed of both inorganic and organic compounds that are insoluble. This layer helps to broaden the voltage range of the system, making it possible for the redox reaction of energy storage to occur (34). The SEI layers serve as a protective barrier for hard carbon anodes by preventing direct contact with the electrolyte. However, they still permit the movement of ions through the SEI layers, making them a type of pure ionic conductor (35).

The formation behaviours of SEI are quite complex and affected by various factors, including the properties of the electrode materials and electrolytes. When ester-based electrolytes degrade, their inorganic and organic components tend to mix randomly without any specific pattern. On the other hand, in ether-based electrolytes, the degraded inorganic particles are designed to be evenly dispersed within a continuous phase of organic components (7). Therefore, understanding the mechanism of SEI formation during initial cycles and the impact of hard carbon structures on SEI formation requires further research. Achieving low first cycle loss and a stable SEI during the very first, and subsequent cycles requires a suitable solution as well as electrode materials (34).

2.7. Electrolytes

To create a stable SEI layer, it is crucial to choose an electrolyte which creates just that during the first cycle of charging. The creation of a good electrolyte has been a bottleneck in the development of low first cycle irreversible loss, especially for SIBs. Electrolytes derived from those of LIBs have been investigated, where most of the nonaqueous electrolytes belongs to the organic esters and ethers. Carbonate ester-based electrolytes has also been looked at due to their higher electrochemical stability and its ability to dissolve Li^+ and Na^+ salts.

Unfortunately the electrolyte optimized for the anode is usually incompatible with the one optimized for the cathode and vice versa, leading to difficulties in developing a generally optimized electrolyte for the SIBs (36).

LIBs needs the electrolyte solvent to be polar enough to dissociate a salt, while being electrochemically inert in a wide potential range of about 0 – 5.0 V vs. Li. These requirements narrows down the choice of solvents capable for use down to a few families of aprotic organic compounds, mainly being organic esters of carbonic acid, along with ethylene carbonate (37). It has been shown that the solvent ratio has negligible effect on the performance of both the cathode and the anode, but it does however affect the issues of thermal compatibility and ionic conductivity (38).

3. Discussion

3.1. Battery structure

One important aspect to consider when comparing SIBs and LIB structures is the difference in their ion size. Na-ions are larger than Li-ions, which affects the materials used in the battery. Due to their larger interlayer spacing of hard carbons, they are often used as anodes in SIBs, because of their ability to accommodate the larger Na-ions. In contrast, graphite is the most used anode material in LIBs due to its ability to intercalate Li-ions. It is important to note that the material being used in the anode material needs to fulfil many criteria to be a successful anode, where the interlayer spacing is one of the more impactful ones.

Another key component of both SIBs and LIBs is the cathode material. In LIBs, the cathode material is often a lithium transition metal oxide, such as LiFePO_4 or $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ ($x+y+z = 1$). Cathodes containing cobalt has a wide range of applications, but is restricted due to their high cost and lack of thermal stability (39). As LIBs are the most widespread commercially used battery as of today, it is being researched to find ways of stabilizing its effects during higher temperatures (40). In SIBs, the most common cathodes are phosphates, oxides and Prussian blue analogs (41). However, SIBs also have the potential to use cathode materials that are not compatible with LIBs, such as sodium vanadium phosphate ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$), which has a higher energy density than NaFePO_4 (42).

In conclusion, while SIBs and LIBs share some similarities in their structures, such as the use of anodes and cathodes, the differences in ion size and materials used require careful consideration in the design and optimization of these batteries. Additionally, the formation of the SEI and the choice of electrolyte can significantly impact battery performance and must be carefully chosen and optimized for each application.

3.2. Anode material

Anode materials play a crucial role in the performance and stability of both LIBs and SIBs. Graphite anodes are the most widely used anode material in LIBs due to their high capacity, low cost, lightweight and good cycling stability. However, they also have their drawbacks such as first cycle irreversible loss of capacity caused by the SEI formation. SIBs using hard carbon as anode material have some advantages when it comes to their low cost, relatively high capacity and environmental friendliness. Hard carbon anodes are currently seen as the

best anode for SIBs (as of 2023), as they can be made from organic waste materials. SIBs struggle even more than LIBs when it comes to first cycle irreversible loss, because of the formation of a more random SEI layer on the anode. It is worth mentioning that if there is no redox capacity, the decrease in potential can be attributed to the discharge of an electric double layer. The slight increase in the potential during pause times indicates that the SEI is not stable enough and dissolves in the electrolyte (Ma et al., 2021). Poor cycling stability also hinders their wider application (44). Moreover, hard carbon anodes made from different materials may exhibit different properties, making their manufacturing and optimization more specific to their use (20).

While graphite anodes remain the most widely used in LIBs, hard carbon anodes offer a low-cost and environmentally friendly solution for the SIBs. The microporosity of hard carbon anodes leads to a higher surface area and lower density, which can impact their performance and stability. The formation of SEI layers and the possibility of redissolving of Na compounds in the electrolyte, as well as optimizing cycling stability and first cycle loss are challenges that need to be addressed to realize the full potential of hard carbon anodes in SIBs, as they offer a low-cost and environmentally friendly battery (44).

3.3. Graphite and hard carbon properties, structure and composition

A lot of a materials property is determined by its crystal structure, stacking and composition. Graphite and hard carbon are two different forms of carbon that have unique structures and properties. Graphite is a sp^2 hybridized form of carbon and consists of layers of graphene that are held together by weak van der Waals forces. These layers can stack in three different modes, with the AA-stacked graphite having the highest density of free electrons and holes, the widest energy dispersion, and the largest band overlap (21). On the other hand, hard carbon is a type of carbon material that cannot be graphitized even when exposed to high temperatures, which also has its advantages such as maintaining its structure under temperatures that would change the structure of other materials. The structure of hard carbon includes curved graphene sheets that cannot be flattened or unfolded, making it unable to be stacked into graphite (26).

The composition of graphite and hard carbon also differs. Graphite is composed of layers of graphene that as mentioned are held together by van der Waals forces. Its interlayer spaces

can be easily intercalated with ions, because of its layer-layer distance of 3.35 Å, forming graphite intercalation compounds (21). In contrast, hard carbon is composed of small graphene sheets, amorphous regions containing defects, and pores. The layer-layer distance in hard carbon is around 3.7-4.0 Å, which is larger than the layer-layer distance in graphite (28). One would assume this is needed for the bigger sodium-ions to fit and make intercalation possible, but potassium ions (K^+) can intercalate into graphite forming KC_8 with a theoretical capacity of 279 mAhg⁻¹. Graphite shows very little capacity for sodium however, storing it as NaC_{186} (45) or NaC_{64} (46) exhibiting 12 and 35 mAhg⁻¹, respectively (47).

The properties of graphite and hard carbon are also distinct. Graphite has high electrical conductivity, thermal conductivity, and lubricity due to the high density of free electrons and holes in the AA-stacked graphite. The stacking pattern of graphite layers determines its band structures and density of states, which affect its conductivity and electrochemical performance as an anode (21). When lithium ions are intercalated into the graphite lattice, the lattice expands to accommodate the larger size of the Li^+ ions. This expansion is anisotropic and mainly occurs along the axis that is perpendicular to the graphene layers. The intercalation of Li^+ ions into graphite sheets leads to a reversible redox reaction and the formation of Li_xC_6 and Li_xC_{12} , which are stable compounds (48). The layered structure of graphite facilitates the intercalation of lithium ions, leading to theoretical maximum specific capacity of up to 372 mAh g⁻¹ (49).

The properties of hard carbon may vary depending on the type of hard carbon and its precursor. Hard carbon has lower electrical conductivity and thermal conductivity compared to graphite, but it has high specific capacity, good cycle stability, and excellent rate capability (50). By using a hard carbon anode made from a mixture of pitch and phenolic resin it has been found that a battery with high specific capacity of 284 mAh g⁻¹ with a capacity retention of 94% after 100 cycles and a first cycle irreversible loss of 12% is possible to make (50). This leads to LIBs having a higher energy density than SIBs (51).

3.4. Solid electrolyte interphase (SEI)

Both LIBs and SIBs require the formation of a SEI on the anode surface during the first cycle of charging and discharging. The SEI is crucial for stabilizing the battery performance and preventing further electrolyte decomposition and thus causing the battery to malfunction.

However, the SEI formation behaviours are quite complex and depend on multiple factors, such as the properties of the electrode materials and the electrolyte used. In both SIBs and LIBs, the electrolyte composition can affect the SEI formation and subsequently impact the first cycle loss. The SEI layer is important in the overall performance and lifetime of the battery by enabling stable and efficient cycling of the battery, even when it comes at the cost of irreversible loss of capacity (30).

In the case of both the LIBs and the SIBs, the SEI layer forms on the anode surface. The graphite anode in LIBs has a tightly packed and ordered crystal structure, which allows for the formation of a more uniform and stable SEI layer. The graphite anode also has a relatively low volume change during charging and discharging, which allows for the SEI layer to remain intact throughout the battery's lifetime (8). To minimize the irreversible capacity loss during the first cycles the chemical composition of the SEI should contain stable and insoluble compact inorganic compounds, such as Li_2CO_3 , LiF and Li_3PO_4 , rather than metastable organic ones (30), (52). Studies has showed that organic compounds are more present towards the electrolyte, while inorganic compounds are more present at the anode (53). This has proved important in confining the loss of lithium inventory.

The hard carbon anode in SIBs has a disordered and porous structure, which can result in a less uniform and stable SEI layer. The hard carbon anode also undergoes a significant volume change during charging and discharging, which can cause the SEI layer to crack and become less effective over time. Because of this it has been hard to create a protective SEI, but by using a pre-engineered artificial SEI form an ester-based electrolyte the hard carbon anode has been stabilized successfully. The SIB created had a capacity of 200 mAh g^{-1} that was retained for over 1000 cycles without detectable capacity loss (44). The hard carbon anode's porous structure can be advantageous to the graphite anodes, as it allows for a higher capacity and better rate capability, but it has shown to be more difficult to stabilize.

3.5. First cycle irreversible loss

In both LIBs and SIBs, the first cycle irreversible loss is caused mostly by the formation of a SEI layer on the anode. The process that forms the SEI layer, when the first charging/discharging takes place, consumes active lithium ions and is the main influencing factor in first cycle irreversible loss in LIBs (16). A generally stable SEI is mainly formed

during the first cycle, and consumes about 10% ~ 20% of the initial capacity. This should provide the cycling performance expected by a graphite anode in a LIB (54).

The first cycle irreversible loss in SIBs has proven to be a major problem with any kind of anode material. The hard carbon anode has struggled with high first cycle irreversible loss and rapid capacity decline, in large parts because of the SEI formation. By controlling the formation of the SEI, researchers have increased the efficiency of SIB anodes, although the composition of SEI and how it evolved are unknown (55).

4. Conclusion

First cycle irreversible loss is a phenomenon in both LIBs and SIBs which causes a reduction in capacity after the very first cycle of charging. This is a disadvantage and not wanted in the battery. Unfortunately the majority of the charge loss comes from the formation of the SEI layer, which is crucial for the battery's anode in these cases to not degrade further and to stabilize the performance (30). With this information in mind, the construction of a better SEI is crucial in the research of minimizing first cycle irreversible loss in both LIBs and SIBs. It is also worth mentioning the necessity to develop complementary battery technologies alongside LIBs to cover for the rising demand. SIBs are good candidates for replacing LIBs in sectors where price is more crucial than energy density, because of their low price, sustainability and abundant storage capacity (56). This stresses the goal of lowering the irreversible first cycle loss, by evolving the knowledge of how to optimize SEI further, and especially in the case of SIBs as it is currently a big bottleneck (57), (55).

As of now the SEI layer on LIBs are more stable and causes less first cycle irreversible loss than the SEI layer on SIBs, but the LIBs will need help to meet the increasing demand of energy storage. Both price and environmental friendliness are key factors in developing such an energy storage, and SIBs would as mentioned be a great contender if it's first cycle irreversible loss got reduced. To help SIBs reduce irreversible first cycle loss, an optimized SEI is crucial. Researchers are looking into ways of creating a nanostructure SEI, creating a double-layer nano SEI film consisting of an inner layer of inorganic matter and an outer layer of organic matter. This SEI would lead to both long cycle life, outstanding performance and low first cycle irreversible loss (58).

There comes as no surprise that the SIBs needs more research to be able to coexist with the standard LIBs, let alone replace them, in majority because of their first cycle irreversible loss. Research has come a long way of improving the flaws of the SIBs, specifically when it comes to evolving the SEI, and hence the gap between LIBs and SIBs are closing. Hopefully, with evolving SIB technology, we can develop batteries according to the applications needs, for example energy density vs. price, and SIBs could have their place and use alongside LIBs in the future.

References

1. Nayak PK, Yang L, Brehm W, Adelhelm P. From lithium-ion to sodium-ion batteries: advantages, challenges, and surprises. *Angew Chem Int Ed*. 2018;57(1):102–20.
2. Sandhya CP, John B, Gouri C. Lithium titanate as anode material for lithium-ion cells: a review. *Ionics*. 2014;20:601–20.
3. Zhang N, Deng T, Zhang S, Wang C, Chen L, Wang C, et al. Critical Review on Low-Temperature Li-Ion/Metal Batteries. *Adv Mater*. 2022;34(15):2107899.
4. Ponrouch A, Monti D, Boschini A, Steen B, Johansson P, Palacín MR. Non-aqueous electrolytes for sodium-ion batteries. *J Mater Chem A*. 2015;3(1):22–42.
5. Zhang WJ. A review of the electrochemical performance of alloy anodes for lithium-ion batteries | Elsevier Enhanced Reader [Internet]. [cited 2023 Mar 14]. Available from: <https://reader.elsevier.com/reader/sd/pii/S0378775310011699?token=9A02AB3FA09C19D7CCFD95622B208586719A441DF28D80A281FA42C8FC9A7DF10480243187807799E38A0056E40AAEAB&originRegion=eu-west-1&originCreation=20230314125908>
6. Cao Z, Xu P, Zhai H, Du S, Mandal J, Dontigny M, et al. Ambient-Air Stable Lithiated Anode for Rechargeable Li-Ion Batteries with High Energy Density. *Nano Lett*. 2016 Nov 9;16(11):7235–40.
7. Saurel D, Orayech B, Xiao B, Carriazo D, Li X, Rojo T. From Charge Storage Mechanism to Performance: A Roadmap toward High Specific Energy Sodium-Ion Batteries through Carbon Anode Optimization. *Adv Energy Mater*. 2018;8(17):1703268.
8. An SJ, Li J, Daniel C, Mohanty D, Nagpure S, Wood DL. The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon*. 2016 Aug 1;105:52–76.
9. Deng D. Li-ion batteries: basics, progress, and challenges. *Energy Sci Eng*. 2015;3(5):385–418.
10. Luo W, Chen X, Xia Y, Chen M, Wang L, Wang Q, et al. Surface and Interface Engineering of Silicon-Based Anode Materials for Lithium-Ion Batteries. *Adv Energy Mater*. 2017 Dec;7(24):1701083.
11. Liu L, Xie F, Lyu J, Zhao T, Li T, Choi BG. Tin-based anode materials with well-designed architectures for next-generation lithium-ion batteries. *J Power Sources*. 2016 Jul 30;321:11–35.
12. Obrovac MN, Christensen L. Structural changes in silicon anodes during lithium insertion/extraction. *Electrochem Solid-State Lett*. 2004;7(5):A93.
13. Verbrugge MW, Baker DR, Xiao X, Zhang Q, Cheng YT. Experimental and theoretical characterization of electrode materials that undergo large volume changes and application to the lithium–silicon system. *J Phys Chem C*. 2015;119(10):5341–9.
14. Liang B, Liu Y, Xu Y. Silicon-based materials as high capacity anodes for next generation lithium ion batteries. *J Power Sources*. 2014;267:469–90.

15. Nzereogu PU, Omah AD, Ezema FI, Iwuoha EI, Nwanya AC. Anode materials for lithium-ion batteries: A review. *Appl Surf Sci Adv.* 2022 Jun 1;9:100233.
16. Lin YX, Liu Z, Leung K, Chen LQ, Lu P, Qi Y. Connecting the irreversible capacity loss in Li-ion batteries with the electronic insulating properties of solid electrolyte interphase (SEI) components. *J Power Sources.* 2016 Mar;309:221–30.
17. Yuqin C, Hong L, Lie W, Tianhong L. Irreversible capacity loss of graphite electrode in lithium-ion batteries. *J Power Sources.* 1997 Oct 1;68(2):187–90.
18. Wang Z, Selbach SM, Grande T. Van der Waals density functional study of the energetics of alkali metal intercalation in graphite. *RSC Adv.* 2013 Dec 16;4(8):4069–79.
19. Thompson M, Xia Q, Hu Z, Song Zhao X. A review on biomass-derived hard carbon materials for sodium-ion batteries. *Mater Adv.* 2021;2(18):5881–905.
20. Lei H, Li J, Zhang X, Ma L, Ji Z, Wang Z, et al. A review of hard carbon anode: Rational design and advanced characterization in potassium ion batteries. *InfoMat.* 2022;4(2):e12272.
21. Nishi Y. 2 - Past, Present and Future of Lithium-Ion Batteries: Can New Technologies Open up New Horizons? In: Pistoia G, editor. *Lithium-Ion Batteries* [Internet]. Amsterdam: Elsevier; 2014 [cited 2023 Apr 21]. p. 21–39. Available from: <https://www.sciencedirect.com/science/article/pii/B9780444595133000029>
22. Zhang H, Yang Y, Ren D, Wang L, He X. Graphite as anode materials: Fundamental mechanism, recent progress and advances. *Energy Storage Mater.* 2021 Apr 1;36:147–70.
23. Schmuch R, Wagner R, Hörpel G, Placke T, Winter M. Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat Energy.* 2018 Apr;3(4):267–78.
24. Pillot C. *The Rechargeable Battery Market and Main Trends 2011-2020.* 2018;
25. *Critical raw materials* [Internet]. [cited 2023 Apr 27]. Available from: https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en
26. Cowlard FC, Lewis JC. Vitreous carbon — A new form of carbon. *J Mater Sci.* 1967 Nov 1;2(6):507–12.
27. Zhao LF, Hu Z, Lai WH, Tao Y, Peng J, Miao ZC, et al. Hard Carbon Anodes: Fundamental Understanding and Commercial Perspectives for Na-Ion Batteries beyond Li-Ion and K-Ion Counterparts. *Adv Energy Mater.* 2021;11(1):2002704.
28. Xiao B, Rojo T, Li X. Hard Carbon as Sodium-Ion Battery Anodes: Progress and Challenges. *ChemSusChem.* 2019 Jan 10;12(1):133–44.
29. Sarkar A, Manohar CV, Mitra S. A simple approach to minimize the first cycle irreversible loss of sodium titanate anode towards the development of sodium-ion battery. *Nano Energy.* 2020 Apr 1;70:104520.

30. Verma P, Maire P, Novák P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochimica Acta*. 2010 Sep 1;55(22):6332–41.
31. Heiskanen SK, Kim J, Lucht BL. Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries. *Joule*. 2019 Oct 16;3(10):2322–33.
32. Joho F, Rykart B, Blome A, Novák P, Wilhelm H, Spahr ME. Relation between surface properties, pore structure and first-cycle charge loss of graphite as negative electrode in lithium-ion batteries. *J Power Sources*. 2001 Jul 1;97–98:78–82.
33. Goodenough JB, Kim Y. Challenges for Rechargeable Li Batteries. *Chem Mater*. 2010 Feb 9;22(3):587–603.
34. Xie F, Xu Z, Guo Z, Titirici MM. Hard carbons for sodium-ion batteries and beyond. *Prog Energy*. 2020 Sep;2(4):042002.
35. Komaba S, Murata W, Ishikawa T, Yabuuchi N, Ozeki T, Nakayama T, et al. Electrochemical Na Insertion and Solid Electrolyte Interphase for Hard-Carbon Electrodes and Application to Na-Ion Batteries. *Adv Funct Mater*. 2011;21(20):3859–67.
36. Eshetu GG, Elia GA, Armand M, Forsyth M, Komaba S, Rojo T, et al. Electrolytes and Interphases in Sodium-Based Rechargeable Batteries: Recent Advances and Perspectives. *Adv Energy Mater*. 2020;10(20):2000093.
37. Xu K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem Rev*. 2014 Dec 10;114(23):11503–618.
38. Zhang SS, Jow TR, Amine K, Henriksen GL. LiPF₆–EC–EMC electrolyte for Li-ion battery. *J Power Sources*. 2002 Apr 20;107(1):18–23.
39. Mahmud S, Rahman M, Kamruzzaman M, Ali MO, Emon MSA, Khatun H, et al. Recent advances in lithium-ion battery materials for improved electrochemical performance: A review. *Results Eng*. 2022 Sep 1;15:100472.
40. Lyu Y, Wu X, Wang K, Feng Z, Cheng T, Liu Y, et al. An Overview on the Advances of LiCoO₂ Cathodes for Lithium-Ion Batteries. *Adv Energy Mater*. 2021;11(2):2000982.
41. Yadav P, Shelke V, Patrike A, Shelke M. Sodium-based batteries: development, commercialization journey and new emerging chemistries. *Oxf Open Mater Sci*. 2023 Jan 4;3(1):itac019.
42. Gu Y, Xiao F, Xu K, Pan X, Li J, Xu C, et al. Outstanding electrochemical performance of sodium vanadium phosphate cathode co-modified by carbon-coating and titanium-doping for Na-ion batteries. *Ceram Int*. 2019 Jun 15;45(9):12570–4.
43. Ma LA, Naylor AJ, Nyholm L, Younesi R. Strategies for Mitigating Dissolution of Solid Electrolyte Interphases in Sodium-Ion Batteries | EndNote Click [Internet]. 2021 [cited 2023 Apr 26]. Available from: https://click.endnote.com/viewer?doi=10.1002%2Fange.202013803&token=WzQwMjc2NzIsIjEwLjEwMDIvYW5nZS4yMDIwMTM4MMDMiXQ.Z-WyTSgXMIBced5sMs_pGNt6PU4

44. Bai P, He Y, Xiong P, Zhao X, Xu K, Xu Y. Long cycle life and high rate sodium-ion chemistry for hard carbon anodes. *Energy Storage Mater.* 2018 Jul 1;13:274–82.
45. Stevens DA, Dahn JR. The Mechanisms of Lithium and Sodium Insertion in Carbon Materials. *J Electrochem Soc.* 2001 Jun 25;148(8):A803.
46. Asher RC. A lamellar compound of sodium and graphite. *J Inorg Nucl Chem.* 1959 May 1;10(3):238–49.
47. Li Y, Lu Y, Adelhelm P, Titirici MM, Hu YS. Intercalation chemistry of graphite: alkali metal ions and beyond. *Chem Soc Rev.* 2019 Aug 27;48(17):4655–87.
48. Mao C, Wood M, David L, An SJ, Sheng Y, Du Z, et al. Selecting the Best Graphite for Long-Life, High-Energy Li-Ion Batteries. *J Electrochem Soc.* 2018 Jun 16;165(9):A1837.
49. Wagner NP, Tron A, Tolchard JR, Noia G, Bellmann MP. Silicon anodes for lithium-ion batteries produced from recovered kerf powders. *J Power Sources.* 2019 Feb;414:486–94.
50. El Moctar I, Ni Q, Bai Y, Wu F, Wu C. Hard carbon anode materials for sodium-ion batteries. *Funct Mater Lett.* 2018 Dec;11(06):1830003.
51. Abraham KM. How Comparable Are Sodium-Ion Batteries to Lithium-Ion Counterparts? *ACS Energy Lett.* 2020 Nov 13;5(11):3544–7.
52. Aurbach D, Levi MD, Levi E, Schechter A. Failure and Stabilization Mechanisms of Graphite Electrodes. *J Phys Chem B.* 1997 Mar 1;101(12):2195–206.
53. Liu W, Liu P, Mitlin D. Review of Emerging Concepts in SEI Analysis and Artificial SEI Membranes for Lithium, Sodium, and Potassium Metal Battery Anodes. *Adv Energy Mater.* 2020 Nov;10(43):2002297.
54. Ng SH, Vix-Guterl C, Bernardo Ph, Tran N, Ufheil J, Buqa H, et al. Correlations between surface properties of graphite and the first cycle specific charge loss in lithium-ion batteries. *Carbon.* 2009 Mar 1;47(3):705–12.
55. Meng J, Jia G, Yang H, Wang M. Recent advances for SEI of hard carbon anode in sodium-ion batteries: A mini review. *Front Chem.* 2022 Sep 20;10:986541.
56. Liu Q, Xu R, Mu D, Tan G, Gao H, Li N, et al. Progress in electrolyte and interface of hard carbon and graphite anode for sodium-ion battery. *Carbon Energy.* 2022;4(3):458–79.
57. Westman K, Dugas R, Jankowski P, Wiczorek W, Gachot G, Morcrette M, et al. Diglyme Based Electrolytes for Sodium-Ion Batteries. *ACS Appl Energy Mater.* 2018 Jun 25;1(6):2671–80.
58. Tan S, Yang H, Zhang Z, Xu X, Xu Y, Zhou J, et al. The Progress of Hard Carbon as an Anode Material in Sodium-Ion Batteries. *Molecules.* 2023 Jan;28(7):3134.