

Electrode/Electrolyte Interphases of Sodium-Ion Batteries

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Abstract: The performance of sodium-ion batteries largely depends on the presence and properties of passive films formed on the electrode/electrolyte interfaces. Passive films on negative electrodes inevitably result from the reduction in electrolyte components (solvent and salt anion). They have the properties of a solid electrolyte with sodium ion conductivity and are insulators in terms of electronic conductivity. Usually, they are called SEI—solid electrolyte interphase. The formation of SEI is associated with the consumption of a certain charge, which is an irreversible capacity. Passive films on the surface of positive electrodes (CEI—cathode electrolyte interphase) arise as a result of electrolyte oxidation. The present review summarizes the literature of the recent 15 years concerning the effects of electrode nature (hard carbon, other carbon materials, various metals, oxides, chalcogenides, etc.), electrolyte composition, and other factors on composition and properties of SEIs in sodium-ion batteries. Literary data on CEIs are reviewed as well, although their volume is inferior to that of data on SEIs.

Keywords: sodium-ion batteries; solid-electrolyte interphase; cathode interphase; electrolyte reduction; sodium metal; hard carbon; carbonaceous materials; oxides; chalcogenides; anodes; cathodes



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1. Introduction

One of the most important notions inherent in lithium-ion batteries is the concept of a passive film on the negative electrode, commonly called a solid electrolyte interface (SEI) [1]. Actually, the concept of SEI was formulated long before the advent of lithium-ion batteries in connection with the question of the kinetic stability of metallic lithium in aprotic electrolytes [2,3]. Because it is the most negative metal, lithium reduces the electrolyte (primarily an aprotic solvent) and simultaneously corrodes. Thus, lithium is thermodynamically unstable in aprotic electrolytes. Under certain conditions, insoluble electrolyte reduction products form a passive film on the lithium surface, which has the properties of a solid electrolyte with lithium-ion conductivity and negligible electronic conductivity. The presence of this film (SEI) does not prevent the flow of the current-generating process, namely the anodic dissolution of lithium (for rechargeable batteries, both anodic dissolution and cathodic reduction in lithium) but prevents direct contact of lithium with the electrolyte and the reduction in the latter. The electrolyte reduction is an undesirable (parasitic) process, and the electricity expended in this process represents an irreversible capacity loss. A good SEI contributes to minimizing irreversible capacity, i.e., improving battery performance in general.

Later it was found that SEI is formed not only on the metal lithium electrode but also on the negative electrodes of lithium-ion batteries, the operating potential of which is quite negative. The formation of SEI on electrodes made of carbon materials has been investigated in length.

On the positive electrodes of lithium-ion batteries, which are characterized by rather high values of operating potentials, electrolyte oxidation is possible with the formation of corresponding passive films. Such films were named cathode electrolyte interphase (CEI) [4]. (The term solid permeable interphase (SPI) [5] is less commonly used).

The very existence and role of SEI and CEI in sodium-ion batteries are taken for granted. There are much fewer studies of SEI and CEI in the sodium system than similar studies in the lithium one, but there are still several reviews on sodium SEI and CEI [6–15].

The principle of SEI functioning is depicted in Figure 1. Coarse-solvated Li^+ ions approach an electrode surface coated with SEI. They cannot penetrate SEI, but after desolvation, small Li^+ ions are transferred through SEI and fit in the crystal lattice. SEI consists of inorganic particles embedded in an organic (polymer, oligomer) matrix.

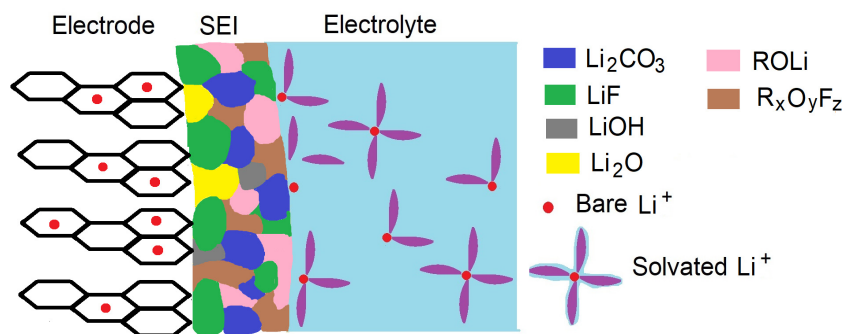


Figure 1. Schematic of SEI functioning.

The composition and properties of SEI and CEI depend on many factors, including the nature of the electrode material, the nature of the electrolyte and the presence of additives in the electrolyte, the pre-history of the electrode, etc.

2. SEI on Sodium Metal

Sodium metal is not used in sodium-ion batteries (except for all-solid-state ones). Sodium metal electrodes are intended for sodium-oxygen [16], sodium-sulfur [17], sodium-carbon dioxide [18], and so on systems. However, it is reasonable to consider the formation of SEIs on sodium metal, especially considering the difference between such SEIs and SEIs on lithium metal. Although lithium and sodium are very similar in physical and chemical properties, and lithium and sodium power sources have a similar principle of operation, their electrochemical behavior is very different. The nucleation and growth of sodium dendrites are more difficult than for lithium ones due to the higher energy barrier and the slowness of processes with sodium compared to lithium. Accordingly, sodium deposition overpotential is typically higher than for lithium, resulting in a lower discharge voltage for power sources with sodium electrodes. At the same time, sodium is more reactive with respect to electrolyte than lithium.

At the first contact of sodium metal with an electrolyte under open circuit conditions, a continuous primary passive film is formed on its surface. With further cathodic polarization, the growth of sodium dendrites begins, mainly in the places of cracks and other defects in the passive film. The interaction of the surface of the dendrites with the electrolyte leads to the well-known phenomenon of encapsulation and the removal of part of the sodium from the further electrochemical process. In contrast to lithium needle-like dendrites, sodium dendrites have a branched, bushy, or mossy shape with a much more developed surface [19]. Thus, natural SEIs on sodium has a much lower protective ability than on lithium [10–12,19–23]. For example, it was shown in [12] that the potential of a lithium electrode at both anode and cathode current density of 1 mA/cm^2 in a 1 M LiPF_6 in a mixture of ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) retains a value that does not change with time, while the potential of a sodium electrode at the same current densities in a 1 M NaClO_4 solution in the same solvent oscillates with a large amplitude. These oscillations point to the continuous destruction and healing of SEI on sodium under these conditions. Moreover, it turned out that SEIs on sodium is much more soluble in the electrolyte than SEIs in lithium systems [24]. It was shown in [25] that, under open circuit conditions, the impedance of the interface between sodium metal and an electrolyte (1 M NaPF_6 in a mixture of EC with dimethyl carbonate (DMC) or in a

mixture of EC:PC:DMC) is way more than the impedance of the interface between lithium metal and a similar electrolyte. Unlike the lithium system, the impedance in the sodium system increases continuously with time. That is why repeated attempts have been made to create “artificial” SEIs on sodium metal by optimizing the composition of the electrolyte, including using various additives to the electrolyte.

The properties of SEI formed in carbonate electrolytes depend markedly on the electrolyte composition, in particular, on the solvent nature. For example, it was shown in [26] that the polarization of a sodium electrode in 1 M NaClO₄ in pure PC significantly exceeds that in 1 M NaClO₄ in a PC:EC mixture.

As a rule, SEI formed in carbonate electrolytes has a much lower protective ability than SEI in ether electrolytes [10,12,22]. For example, it was shown in [22] that the replacement of the traditional carbonate electrolyte with NaPF₆ solutions in glymes (mono-, di-, and tetraglyme) makes it possible to carry out the cathodic deposition of sodium without SEI destruction and without the formation of dendrites. SEIs, in this case, contain Na₂O and NaF as mineral constituents and sodium alkoxides (RCH₂ONa) as organic constituents. It was emphasized that the formation of high-quality SEI, in this case, is provided by both the solvent and the salt. Replacing sodium hexafluorophosphate with other salts, such as sodium imide, triflate, or perchlorate, while retaining glyme as a solvent, or replacing glyme with carbonates, resulted in SEI that did not prevent dendrite formation. However, in [27–29], the formation of reliable SEIs in a carbonate electrolyte, specifically 1 M sodium difluorooxalatoborate in an EC-DEC mixture, was reported.

Another example of a successful electrolyte for the functioning of a rechargeable sodium electrode is highly concentrated (about 5 M) solutions of sodium bisfluorosulfonylimide (NaFSI) in 1,2-dimethoxyethane (DME) [30], with a high concentration (close to saturation) of NaFSI being an indispensable condition for the formation of high-quality SEI. The authors of [31] came to the same conclusion somewhat earlier. It was shown in [32] that the same effect could be achieved in much less concentrated (1.5 M) NaFSI solutions in mixtures of 1,2-dimethoxyethane (DME) with bis(2,2,2-trifluoroethyl) ether (BTFE). It is high time to stress the fact that the elemental composition of SEI formed in a concentrated solution of NaFSI in DME and in a dilute solution of NaFSI in a DME-BTFE mixture turned out to be almost the same and differed from the composition of SEI formed in a dilute solution of NaFSI in DME (Figure 2). Figure 2 also clearly shows the change in SEI composition with depth. The content of carbon and nitrogen (that is, the organic component) on the surface of the SEI is much greater than at a depth of 10 nm. The ratio of solvents DME:BTFE in the mixture should be from 1:2 to 1:3. A solution of NaFSI in an ionic liquid, tri(isobutyl)methylphosphonium bis(fluorosulfonyl)imide, also proved to be a successful electrolyte [33]. At a NaFSI concentration of 45% in such an electrolyte, dense, high-quality SEIs were formed.

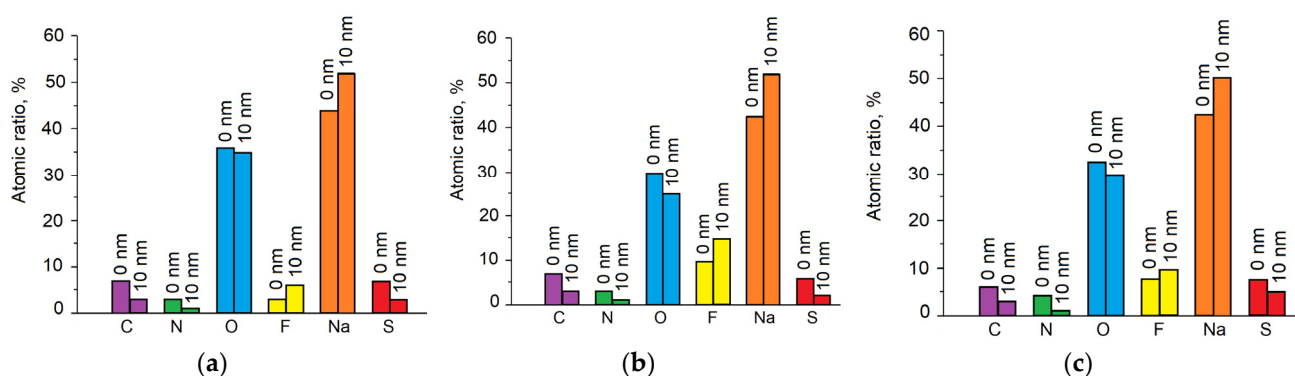


Figure 2. Depth variation in the composition of SEIs formed in different electrolytes. Electrolyte composition: (a)—1.7 M NaFSI in DME, (b)—5.2 M NaFSI in DME, (c)—2.1 M NaFSI in DME:BTFE (1:2).

Somewhat exotic electrolytes that ensure the formation of high-quality SEIs on the surface of sodium metal were proposed in [34]. Here, ammonia-based quasi-ionic liquids were used, having the composition $\text{NaY} \cdot x\text{NH}_3$, where Y is any anion, in particular, $\text{NaI} \cdot 3.3\text{NH}_3$, $\text{NaBH}_4 \cdot 1.5\text{NH}_3$, and $\text{NaBF}_4 \cdot 2.5\text{NH}_3$. These compounds have boiling points of 40, 18, and 10 °C, respectively, and are highly concentrated (7.6, 12.3, and 9.7 M, respectively) solutions of Na^+ in liquid ammonia. (It is not out of place to mention that $\text{NaI} \cdot 3.3\text{NH}_3$, as an electrolyte for primary cells with a sodium anode, was proposed back in 1988 [35]). In [36], a similar electrolyte based on the quasi-ionic liquid $\text{NaAlCl}_4 \cdot 2\text{SO}_2$ is described. In such an electrolyte, SEI is formed on the sodium surface, consisting mainly of NaCl (along with small amounts of Na_2O and Na_2S), and completely prevents the formation of dendrites during cathodic sodium deposition.

As for various additives to the electrolyte, perhaps the most discussed additive is fluoroethylene carbonate (FEC) [37], which has good film-forming properties [38], suppresses the destruction of solvents, and improves the conditions for the electrode process [19,39–42]. The addition of FEC has proven itself well in the lithium system. When used in power sources with a sodium electrode, the concentration of this additive should be increased compared to lithium systems [12]. However, in the literature, one can also find an indication of the negative effect of the addition of FEC on the properties of SEI on sodium metal [30,43]. (But, for example, in [43], it is shown that the harmful effect of FEC can be neutralized by the addition of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether). The addition of FEC leads to a significant enrichment of SEI with sodium fluoride, which was shown both by theoretical calculations [44–47] and by direct experiments [19,41,42]. Another important additive to the electrolyte that provides high-quality SEI on sodium metal is sodium sulfide, more precisely, sodium polysulfides [48].

In general, the nomenclature of additives that improve SEI on sodium metal is not at all systematic. For example, potassium bis(trifluoromethylsulfonyl)imide was mentioned as a useful additive [49]. (It was assumed that in the presence of TFSI-anions, the composition of SEI would include sodium nitride (Na_3N) and sodium oxynitrides (NaN_xO_y); it is surprising that this idea is not mentioned in work [30], which is especially devoted to the imide electrolyte). In [50], SbF_3 is announced as a useful additive to a concentrated imide electrolyte. Figure 3 vividly shows the effect of SbF_3 additive to the electrolyte on dendrite formation. In the presence of such an additive, a bilayer SEI is formed on the sodium surface. The inner layer consists of a Na-Sb alloy. The outer layer is a regular SEI enriched with NaF (Figure 3c). This bilayer SEI is thinner than the SEI formed in the same electrolyte without the addition of SbF_3 (Figure 3b) and ensures the deposition of a uniform dendrite-free sodium layer. A comparison of Figure 3a,b shows the advantage of the ether electrolyte over the carbonate one.

The authors of [51] propose the addition of NaAsF_6 to carbonate electrolytes. It is indicated that in this case, SEI contains significant amounts of sodium fluoride and O–As–O polymer, and it is this combination that provides high protective properties of SEI. At the same time, authors of [52] postulate the detrimental effect of NaF on the properties of SEI on sodium metal and show that excellent SEI can be obtained in completely fluoride-free electrolytes, for example, in a solution of sodium tetraphenylborate (NaBPh_4) in DME. In [53], tin chloride is proposed as an additive to carbonate electrolytes. It is assumed that in such electrolytes, an Sn–Na alloy is formed on the sodium surface (due to the contact reduction in tin ions), and SEI will be enriched with NaCl. It has also been proposed to apply a thin (sub-nanometer) layer of protective coating to the surface of sodium metal as some kind of “artificial SEI.” These can be layered 2D materials (hexagonal boron nitride, graphene, silicene, germanene, stannene, phosphorene, etc.) [54,55] or composite layers consisting of a polymer (for example, a copolymer of polyvinylidene fluoride with hexafluoropropylene (PVdF-HFP) saturated with an ordinary liquid electrolyte (plasticizer) with a filler of Al_2O_3 nanopowder) [56,57]. Another option for “artificial SEI” is a thin layer of sodium disulfide [58]. To form such an “artificial SEI,” a layer of molybdenum disulfide

is applied to the surface of metallic sodium, which interacts with sodium according to the equation



In [59], it is proposed to use not pure sodium metal but a sodium composite with reduced graphene oxide. In this case, it is not sodium that contacts the electrolyte, but graphene, on the surface of which a stable SEI is formed.

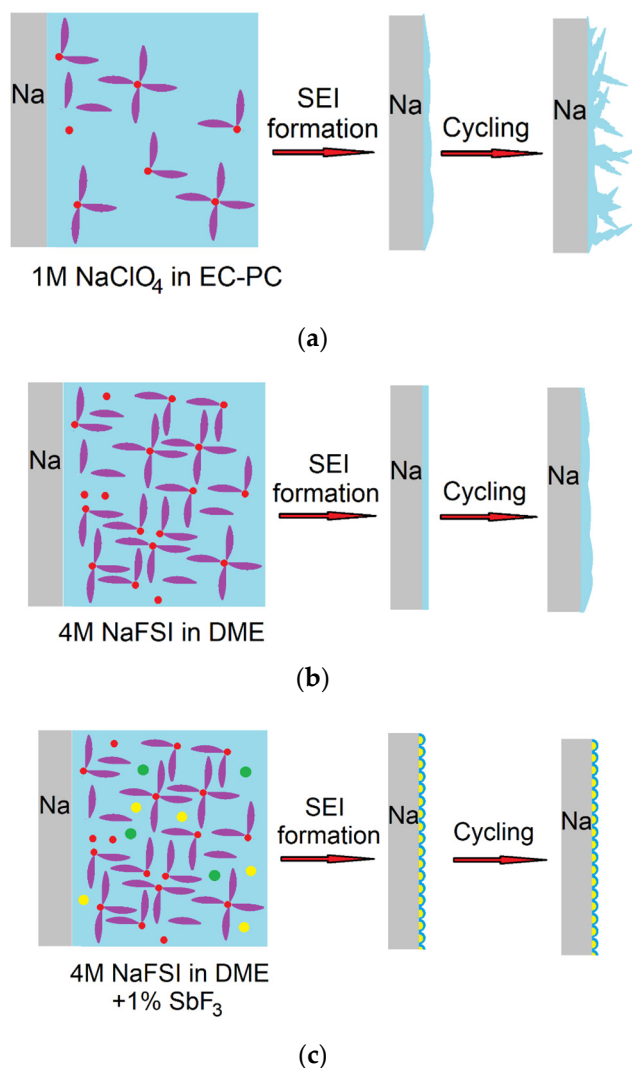


Figure 3. SEI effect on dendrite formation in various electrolytes. (a) a common electrolyte (1 M NaClO₄ in EC–PC mixture), (b) high concentration imide electrolyte (4 M NaFSI in DME), (c) high concentration imide electrolyte with the addition of 1% SbF₃.

3. SEI on Hard Carbon

Of the wide variety of anode materials proposed for sodium-ion batteries, the most popular is hard carbon, the use of which in sodium-ion batteries was first described in [60,61]. In the non-graphitized disordered turbostratic structure of hard carbon, there are various places for sodium insertion (randomly oriented graphene layers with a “house of cards” structure, various defects, and micropores in stacks of graphene layers) [62–64]. As a result, reversible insertion and extraction of sodium occur over a relatively wide range of potentials. The galvanostatic charge curves show two almost straight segments: a decreasing segment in the potential range from about 1.0 to 0.1 V (hereinafter, all potential values are given relative to the sodium electrode) and a flat segment (plateau) from 0.1 to 0.01 V [62,65,66]. It is on the first falling section that the main charge is spent on

the formation of SEI. Figure 4 explains how a comparison of the charge and discharge galvanostatic curves gives a possibility to find the reversible and irreversible capacity of the electrode.

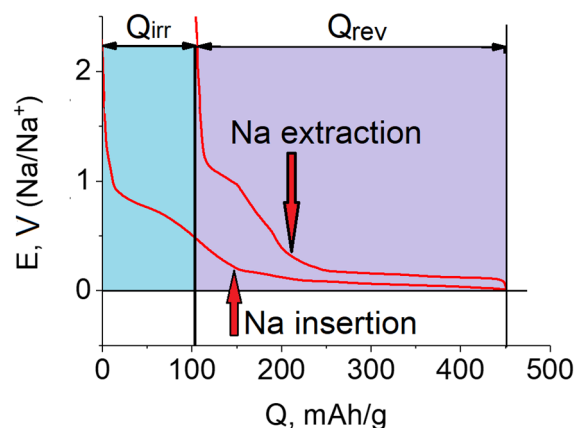


Figure 4. Galvanostatic charge (Na insertion) and discharge (Na extraction) curves of hard carbon electrodes and a scheme for determining reversible (Q_{rev}) and irreversible (Q_{irr}) capacity.

It has been shown in many works that the composition of SEI on hard carbon electrodes substantially depends on the composition of the electrolyte [66–80]. Thus, according to [66], SEI formed in NaClO_4 solution in butylene carbonate (BC) possesses worst protective properties than SEI formed in solutions in EC and PC (Figure 5a). Even more revealing is the comparison of NaClO_4 solutions in mixtures EC:DMC, EC:ethyl methyl carbonate (EMC), and EC:DEC (Figure 5b).

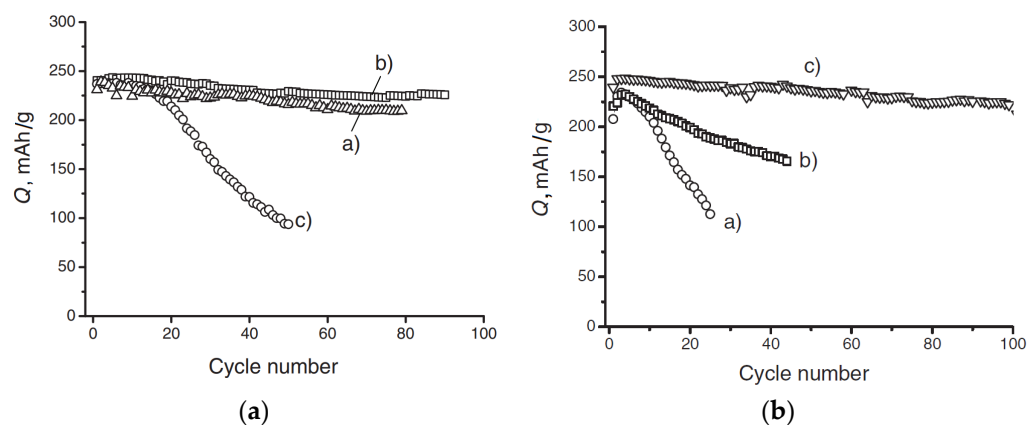


Figure 5. (a) Variation in reversible capacities for hard-carbon electrodes in (a) EC, (b) PC, and (c) BC solution containing 1 mol/dm^3 NaClO_4 tested at 25 mA/g . (b) Reversible capacities for hard-carbon electrodes in (a) EC:DMC (1:1), (b) EC:EMC (1:1), and (c) EC:DEC (1:1) solution containing 1 mol/dm^3 NaClO_4 at 25 mA/g . (Reprinted with permission from [66]. Copyright 2011, Wiley Online Library).

The composition of the electrolyte affects not only the brutto-composition of the SEI but also the distribution of the SEI components over its thickness. Figure 6 shows the fundamental difference between conventional carbonate electrolytes (Figure 6a) and electrolytes based on ionic liquid (Figure 6b).

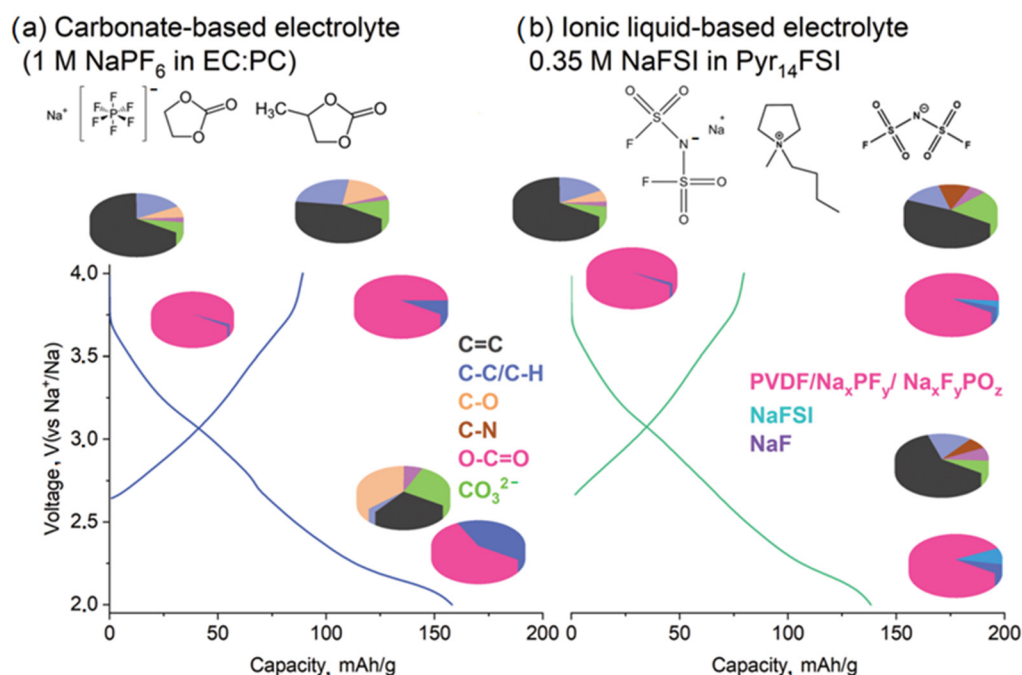


Figure 6. Voltage profile of the 1st cycle and the concentration of the SEI species obtained by fitting C 1s and F 1s photoelectron lines of hard carbon negative electrode tested in (a) carbonate ester-based (1 m NaPF₆ in EC:PC) and (b) ionic-liquid (0.35 m Na[FSI] in [Pyr₁₄][FSI]) electrolyte. (Reprinted with permission from [67]. Copyright 2022, Wiley Online Library, Open Access).

The composition of SEI formed in 1 M solutions of NaPF₆, NaClO₄, NaFSI, NaTFSI (sodium bis(trifluoromethanesulfonyl)imide), and NaFTFSI (sodium fluorosulfonyl(trifluoromethanesulfonyl)imide) in a mixture of EC-DEC was studied in length in [69]. It was shown by X-ray photoelectron spectroscopy (XPS) that the organic part of SEI contains sodium carbonate (Na₂CO₃), sodium alkyl carbonates (ROCO₃Na), sodium alkoxides (RONa), ethylene oxide oligomers, semicarbonates and double sodium alkyl carbonates formed as a result of the reductive destruction of solvents, and the relative amounts of these components depend on the nature of the salt anion. The nature of the salt anion also affects the density and thickness of SEIs: thicker SEIs are formed in the electrolyte with NaClO₄, while thinner SEIs are formed in the electrolytes with NaPF₆ and NaTFSI. The distribution of organic and inorganic (NaCl, NaF, Na₂CO₃) components over the SEI depth also depends on the nature of the anion. The authors of [70] came to similar conclusions. It is also stated in [76] that double alkyl carbonates constitute the main organic component of SEI on hard carbon.

It was shown in [71] that, in a solution of sodium tetrphenylborate in DME, quite stable SEIs are formed on hard carbon electrodes (as well as on sodium metal [52]), which do not contain fluorine compounds and ensure electrode cycling at current densities up to 6 A/g. The behavior of hard carbon in carbonate-based (1 M NaClO₄ in an EC-PC mixture) and ether-based (1 M NaClO₄ in a mixture of tetraglyme with DME) electrolytes were compared in more detail in [80]. It was found that in the former case, loose, non-continuous SEIs, whereas in the latter case, thin, dense, continuous SEIs of uniform thickness is formed. As a result, in the carbonate electrolyte, the electrode processes proceed with greater polarization. Just as in the case of sodium metal, the composition and properties of SEI on hard carbon depend markedly on the presence of additives in the electrolyte. The most popular additive is again FEC [37,67,70,78,81–83], which promotes the formation of thinner dense SEIs. (Intriguingly, such an additive as vinylene carbonate (VC) turned out to be much less effective in sodium-ion batteries than in lithium-ion batteries [37]). The addition of FEC leads to a significant improvement in the properties of SEIs on hard carbon in those electrolytes in which low-quality SEIs generally form, for example, in solutions of NaClO₄

in plain PC [84]. At the same time, in electrolytes based on an EC-PC mixture, the addition of FEC led to a deterioration in the quality of SEI [63].

The reductive decomposition of FEC was found to proceed with significantly lower activation energy than the propylene carbonate reduction [46,47,85]. This conclusion was made by using the density functional theory (DFT) and the method of molecular dynamics. This very feature determines the easier formation of SEI enriched with sodium fluoride. The efficiency of the addition of FEC was shown to depend on its concentration [81,83]. For 1 M solutions of NaPF₆ in PC and EC:PC mixture, the optimal concentration of FEC is 0.5%. It is also stated in [81] that it is the combination of NaPF₆ with FEC that provides a synergistically successful SEI on hard carbon electrodes.

It is commonly accepted that SEI is formed mainly in the first cycle. However, a number of studies have shown that the evolution of the composition and structure of SEI on hard carbon continues over the initial 10–20 cycles. Such a conclusion, in particular, was made in [76], where it was found that in a solution of 1 M NaTFSI in PC with the addition of 3% FEC, SEI on hard carbon thickens and enriches with sodium carbonate and sodium fluoride over the first 20 cycles.

Other additives that have a beneficial effect on the formation of high-quality SEI on hard carbon include tris(trimethylsilyl)phosphite (TMSP, [(CH₃)₃Si]₃PO₃) [86], 1,3-propanesultone (C₃H₆O₃S) and ethylene sulfate (C₂H₄SO₄) [87], ionic liquids [88–90]. The role of TMSP in improving SEI on hard carbon is that the TMSP additive traps traces of oxygen, moisture, as well as HF and PF₅ in the electrolyte [91,92]. Additives of sulfur-containing 1,3-propanesultone and ethylene sulfate contribute to the formation of sulfates and sulfites (ROSO₂Na and RSO₃Na), which stabilize SEI on hard carbon during long-term cycling. The examples of ionic liquids are 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, and N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [88], N-propyl-N-methylpyrrolidinium bisfluorosulfonylamide [89] and 1-ethyl-3-methylimidazolium bisfluorosulfonylimide [90]. It is worth noting that in all cases, the presence of ionic liquids in the electrolyte contributes to an increase in the mechanical and electrochemical stability of SEI due to a change in its composition, although no quantitative data on the composition of SEI are given.

Somewhat unexpected was the effect of nano-zeolite additions to the active mass of hard-carbon-based electrodes on the SEI characteristics [93]. The replacement of part of the carbon black (as an electrically conductive additive) in the active mass of the electrode with alumina-silicate zeolite Nano-ZSM5 P91 (Zeolite Socony Mobil-5) led to a certain decrease in the thickness and resistance of the SEI. It puzzles why the authors of [93] do not comment on the fact that the replacement of 80% of the electronic conductor (carbon black) with an ionic conductor (zeolite) was not accompanied by a deterioration in the characteristics of the electrode even at elevated currents (up to 5 C).

Attempts have been made to create artificial SEIs on solid carbon. For example, paper [94] describes hard carbon fibers on the surface of which arrays of V₂O₅ nanosheets are grown. The total amount of V₂O₅ was 14–20%. When V₂O₅ nanosheets were deposited, the surface of hard carbon was “healed” (decrease in the density of defects and nanovoids), which ensured the formation of a thinner dense SEI. In [95], it is proposed to deposit an Al₂O₃ layer about 2 nm thick on the surface of hard carbon. Such a layer is applied by atomic layer deposition (ALD) and serves as a sublayer for SEI. The authors showed that the SEI formed on such a sublayer has a lower thickness and a higher ionic conductivity. The alumina sublayer is assumed to slow down the process of electrolyte reduction on the surface of hard carbon. Amorphous (soft) carbon coatings obtained from coal tar pitch exert approximately the same effect [96,97].

In general, the composition and properties of SEIs formed on hard carbon are highly dependent on the state of its surface. As a rule, the less defective the surface and the lower the porosity of the surface layer, the perfect SEIs are formed on such surfaces [98–100]. In the synthesis of hard carbon by pyrolysis of various precursors, the state of the surface significantly depends on the temperature and mode of pyrolysis. Thus, it was shown in [98] that when hard carbon is obtained by pyrolysis of peat, samples synthesized at a tempera-

ture of 1400 °C are characterized by the maximum reversible and minimum irreversible capacity and, accordingly, the thinnest and densest SEI. In [100], it was found that at a constant temperature of sucrose pyrolysis, the surface of the resulting hard carbon is more perfect (defect-free), and the slower the heating during pyrolysis occurs. A somewhat different conclusion was formulated in [101], where it was found that thinner and more perfect SEIs are formed on microporous hard carbon than on samples with low porosity.

An original method for stabilizing SEI on hard carbon is described in [102]. Here it is proposed to carry out preliminary short-term treatment of the surface of hard carbon in oxygen plasma [103,104]. In this case, oxygen-containing functional groups are formed on the carbon surface, and the surface itself becomes hydrophilic. On such a surface, very thin SEIs are formed with negligible irreversible capacitance.

Some interesting observations were reported in [105]. It is shown here that dense thin (8 nm) SEIs are formed on electrodes made of hard carbon obtained by pyrolysis of longan peel at room temperature, providing stable cycling with a sufficiently high reversible capacity. Thicker (21 nm) SEIs are formed on the same electrodes at a temperature of −20 °C, which leads to strong degradation during cycling (capacity decreased from 280 to 80 mAh/g in 5 cycles). However, upon subsequent heating to room temperature, the SEI was transformed, i.e., it returned to its previous thickness with a simultaneous increase in capacity up to 250 mAh/g. The expected results on the effect of current density during the charging of electrodes based on hard carbon are reported in [106]. It is shown here that increasing the cathode current density leads to the formation of thinner perfect SEIs. Thus, according to the data of electrochemical impedance spectroscopy, the total electrolyte, and SEI resistance, corresponding to the active component of the impedance at an infinitely high frequency, was 1.3 Ohm·cm² at a charge with a current of 100 A/g and 15.1 Ohm·cm² at a charge with a current of 1 A/g.

When SEI is formed, a significant charge is consumed on the first cycle, and accordingly, a certain amount of sodium ions is lost from the positive electrode. In order to compensate for this loss, it is recommended that the electrode, in particular, a hard-carbon-based one [107], be pre-sodiated. A simple but effective method of pre-sodiation consists in spraying a sodium naphthalene (Naph-Na) solution onto a carbon electrode. Figure 7a shows how the first charge curve changes upon pre-sodiation: open circuit voltage shifts from 2.35 V to 0.75 V, and irreversible capacity diminishes by 60 mAh/g. Some interfacial layer with a thickness of ≈20 nm is formed upon pre-sodiation (Figure 7b). This layer consists of sodium-containing-organic and inorganic compounds, such as sodium alkyl carbonates, sodium carboxylate, sodium carbonate, sodium fluoride, etc.

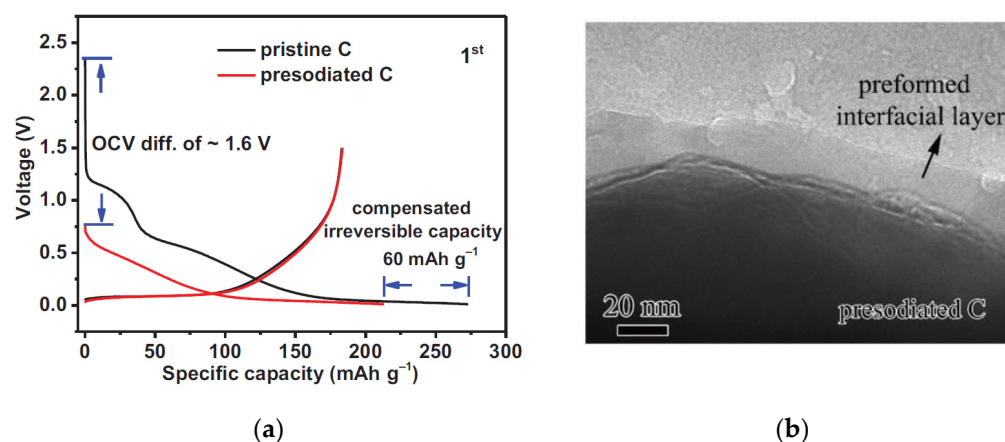


Figure 7. Electrochemical performances of the carbon electrodes with and without presodiation. (a) The voltage-capacity curves of the pristine and presodiated carbon electrode for the first charge/discharge cycle. (b) TEM images of presodiated carbon after immersed in a liquid electrolyte before battery cycling. (Reprinted with permission from [107]. Copyright 2019, Wiley Online Library).

Works [108–110] are devoted to a detailed analysis of the morphology and composition of SEI on hard carbon. Various characteristics of sodium alkyl carbonates are given in [111]. It was found in [112] that SEI on hard carbon grows inward rather than outward, i.e., in the direction from the interface with the electrolyte to the carbon surface.

4. SEI on Other Anode Materials

The list of anode materials in addition to hard carbon is extensive [113] and includes various other forms of carbon [114–145], metals, and their composites with carbon (Sb [146–161], Sn [162–168], Bi [169–175], Cu [176]), silicon [177,178], germanium [179,180] oxides [181–228], chalcogenides [229–243], phosphides and phosphorus composites [244–251], as well as more complex compounds from sodium titanates [252–255], to very exotic compounds [256–260]. As a result, information on each specific material is rather limited.

Some regularities outlined in Sections 1 and 2 happen to be valid also for many other anode materials. For example, the advantages of ether-based electrolytes over carbonate electrolytes have been confirmed for the formation of SEI on graphite [130,142], tin [162,165], bismuth [261], bismuth sulfide [229], bismuth oxychloride [182], $\text{Na}_3(\text{TiOPO}_4)_2\text{F}$ [256], molybdenum and iron sulfides [231,237], TiO_2 [187], etc. A favorable effect of FEC is noted in the formation of SEI on antimony [147–149,153], tin [167], bismuth-carbon composites [169], SnO [222], SnO_2 composites with reduced oxide graphene [224,262], a composite of antimony sulfide with graphene [263], etc. There are examples in the literature of the positive effect of pre-sodiation on the reduction in the irreversible capacity of the first cycle [138,253,264].

At the same time, the composition and structure of SEIs and the features of the processes of their formation and destruction on different materials are, in general, individual. So, on different forms of carbon, even in the same electrolyte, SEIs are formed in several different potential ranges. For example, on carbon nanofibers doped with fluorine and nitrogen, stable high-quality SEIs in an EC-PC-based electrolyte are formed at potentials of about 0.92 and 0.46 V (these values correspond to extrema on voltammograms) [115]. On a carbon material obtained by heat treatment of a mixture of resorcinol and formaldehyde and having the shape of smooth spherical particles (i.e., having a small specific surface area), the SEI formation potential is close to 1.1 V [114]. It is of deep interest that the cited work reports the formation of very thin dense SEIs in an electrolyte based on a mixture of EC-DEC. This fact comes as rather a surprise and contradicts most other works in which SEIs in such an electrolyte have a large thickness and defectiveness (see, e.g., [80]). Thin SEIs on hollow fibers obtained by carbonization of polyaniline is formed at potentials of 0.43 and 1.13 V [117]. At the same time, in the experiments with carbon fibers made by cellulose carbonization, a certain irreversible capacity was registered in the potential range of 0.2 to 0.3 V in EC-PC-based electrolytes [118].

Although graphite is inferior to hard carbon as an anode material for sodium-ion batteries, a sufficient number of studies have been published on the reversible sodium insertion into graphite and the formation of SEI [120,121,127–131,141]. It has been established that, such as lithium, sodium is intercalated into graphite in stages, with the formation of distinct steps on galvanostatic curves [127]. Usually, solvated (or incompletely desolvated) sodium ions are intercalated into graphite. For example, sodium ions bound to one solvent molecule are intercalated from an electrolyte based on diethylene glycol dimethyl ether (DEGDME) [130]. It was shown in [128] that sodium ions solvated by two solvent molecules are reversibly intercalated from a diglyme-based electrolyte. In [141], the formation of SEI was studied in detail upon the sodium intercalation into graphite from a solution of NaFSI in tetraethylene glycol dimethyl ether (TEGDME). Under these conditions, SEI has a thickness of 3 to 8 nm and consists of the reduction products of both the salt anion and the solvent. In [131], a paradoxical conclusion was made that when a graphite electrode is cycled in an electrolyte based on diglyme, SEI is not formed at all. An explanation of this paradox can be found in [140]. Here, using soft X-ray absorption spectroscopy (XAS) it was shown that in an ether-based electrolyte (1 M NaPF_6 in DEGDME), SEI on graphite is

formed during cathodic polarization and is destroyed during subsequent anodic polarization, i.e., shows signs of reversibility. Under the same conditions on disordered (hard or soft) carbon, such reversibility is only partially revealed, and an appreciable part of SEI is formed irreversibly during cathodic polarization and does not undergo transformations during subsequent anodic polarization. In carbonate electrolytes, sodium is not reversibly intercalated into graphite at all [142].

In the example of various carbon electrodes, a certain correlation was found between the specific surface area (or dispersion), and the volume of SEIs formed, i.e., irreversible capacity. For example, it was shown in [124] that when sodium is inserted into carbon xerogels obtained from a resorcinol–formaldehyde mixture and having pores ranging in size from 10 to 200 nm, the irreversible capacity in the first cycle is 85% for the finest and 67% for the largest pores samples. A similar conclusion was made in [125] for porous carbon obtained by carbonization of polyethylene oxide and polystyrene, in [121] for a material obtained by carbonization of peanut hulls, and in [126] for a nanoporous material obtained by carbonization of ZIF-8 zeolite.

The authors of [119,144] describe a carbon material that is, in fact, highly porous (with a specific surface area of more than 1000 m²/g and sizes of micropores from 0.5 to 2 nm and mesopores from 2 to 100 nm) carbon impregnated with sodium. Sodium occupied only part of the pore space. The rest was filled with an electrolyte so that the electrode worked to the entire depth of the active layer. In this case, the layer of oxygen-doped carbon foam was obtained from starch and deposited on a current copper collector. A dense thin SEI containing NaCO₃R, NaF, and Na₂O was formed on such an electrode in a diglyme-based electrolyte, which ensured stable cycling. The outer layer of SEI was enriched in organic components, while the inner layer was enriched in inorganic ones, which is generally typical of SEIs formed in electrolytes based on ethers [120].

The authors of [137] studied electrodes obtained from graphene, on which Al₂O₃ particles about 1 nm in size are fixed. The introduction of these nanoparticles led to a sharp decrease in the defectiveness of graphene layers and the formation of thin homogeneous SEI. Moreover, the presence of such nanoparticles protected the SEI from the harmful effects of HF traces. This effect is similar to that described in [95] for hard carbon.

Of particular interest is the behavior of carbon electrodes in electrolytes based on ionic liquids, i.e., electrolytes that do not contain traditional aprotic solvents [265]. It has been found in many studies that even in electrolytes based on ionic liquids, SEIs are formed on the electrode surface during the first cathodic polarization, the characteristics of which differ from those of “ordinary” SEIs. In particular, the insertion of sodium into electrodes, which are a composite of graphene nanosheets and carbon microspheres in 1 M NaFSI in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PMP-FSI) and in 1 M NaTFSI in N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PMP-TFSI) was studied in [145]. On the voltammograms recorded in 1 M NaFSI in PMP-FSI, a large cathode peak was noted at potentials of about 0.6 V during the first cycle, which the authors identified with the SEI formation due to anion reduction. This peak did not appear in subsequent cycles. According to the XPS analysis, the composition of the SEIs formed in the ionic liquid electrolyte differed from the composition of the SEIs formed in the traditional EC-DEC electrolyte. In the former case, SEIs were enriched in polyolefins ((CH₂)_n) and compounds with S=C=O groups; in the latter case, they had a high content of sodium carbonates and alkyl carbonates and compounds with C–O and C=O groups. It is worth noting that SEIs formed in 1 M NaTFSI in PMP-FSI had a much higher Ohmic resistance and did not provide reliable cycling. A similar conclusion about the composition of SEIs formed in an electrolyte based on PMP-FSI was made in [266].

Antimony has a specific capacity of about 600 mAh/g, is an attractive anode material for sodium-ion batteries. True enough, the working discharge potential of antimony electrodes is noticeably more positive than that of carbon-based electrodes and amounts to 0.7–1.2 V. Even with such positive potentials, SEI is formed on the Sb electrodes, the composition, and properties of which being depended on the nature of the electrolyte.

Noteworthy is that it was shown in [157] that thinner and more reliable SEIs are formed on antimony powder electrodes made using carboxymethyl cellulose as a binder in 1 M NaClO₄ in PC with the addition of FEC than on electrodes made with polyvinylidene fluoride binder (in the first case, the irreversible capacity of the first cycle was half that of the second case).

The properties of SEI on antimony powder electrodes with carboxymethyl cellulose binder were studied in [146] using three electrolytes: 1 M NaClO₄ in PC, 1 M NaPF₆ in PC, and 1 M NaPF₆ in an EC:DMC mixture. All electrolytes were supplemented with 5% FEC. The irreversible capacity of the first cycle was minimal in an electrolyte based on an EC:DMC mixture and maximal in a sodium perchlorate solution.

In the example of antimony electrodes, the conclusion made in the study of carbon electrodes was confirmed that an increase in dispersion is accompanied by an increase in the irreversible capacity of the first cycle [148].

An interesting observation is reported in [152]. Here, cathodic deposition was performed from a solution containing nickel chloride (NiCl₂), L-antimony potassium tartrate (C₈H₄K₂O₁₂Sb₂), boric acid (H₃BO₃), and sodium hypophosphite (NaH₂PO₂). The resulting precipitate was cauliflower-like antimony particles and some (up to 12%) SnNi alloy particles. According to the authors, it was the presence of this alloy that provided dense, high-quality SEIs and high cyclability. In [154], it was found that a change in temperature in the range from 5 to 50 °C leads not so much to a change in the SEI Ohmic resistance on nanocrystalline antimony but to a change in the charge transfer resistance at the interface between the SEI and the electrode. The paper [155] describes an original material that has a garnet structure and consists of secondary spherical particles ranging in size from 2 to 10 microns, each of which contains many yolk-shell particles (antimony core, carbon shell). On such a structure, relatively thick but sufficiently conductive SEIs are formed, which provide damping of volumetric changes during sodium insertion and extraction. A composite consisting of antimony nanoparticles in a porous carbon matrix turned out to be an effective material for the negative electrode of sodium-ion batteries [159]. SEI on such a composite in a carbonate electrolyte with the addition of FEC is formed in a wide range of potentials and ensures stable cycling. Other antimony composites with different carbon materials [160,161] form similar SEIs. Another interesting example of an antimony-containing material is given in [156]. Here, thin plates consisted of antimony nanoparticles with shells of amorphous TiO_{2-x}. We deem it possible to assume that TiO_{2-x} stabilizes the SEI on such electrodes.

The properties of SEIs on tin formed in electrolytes based on alkyl carbonates and based on diglyme were investigated in [162] using cryogenic transmission electron microscopy and XPS. It was shown that in the first case, thick loose SEIs are formed, while in the second case, ultrathin dense SEIs are formed, consisting of a polymer matrix in which amorphous inorganic nanoparticles are dispersed. It is confirmed in [166] that SEIs on tin formed in 1 M NaClO₄ in PC are enriched mainly in sodium carbonate and alkyl carbonates and are partially destroyed by anodic polarization.

The additives of FEC have a significant effect on the properties of SEI. Figure 8a shows the discharge curves on an SnSb-carbon nanotube composite electrode in solutions of NaPF₆ in EC:DEC containing and not containing FEC additives. This Figure also shows the effect of FEC on Coulombic efficiency. With regard to tin electrodes, glyme-based electrolytes also have advantages over carbonate-based ones (Figure 8b).

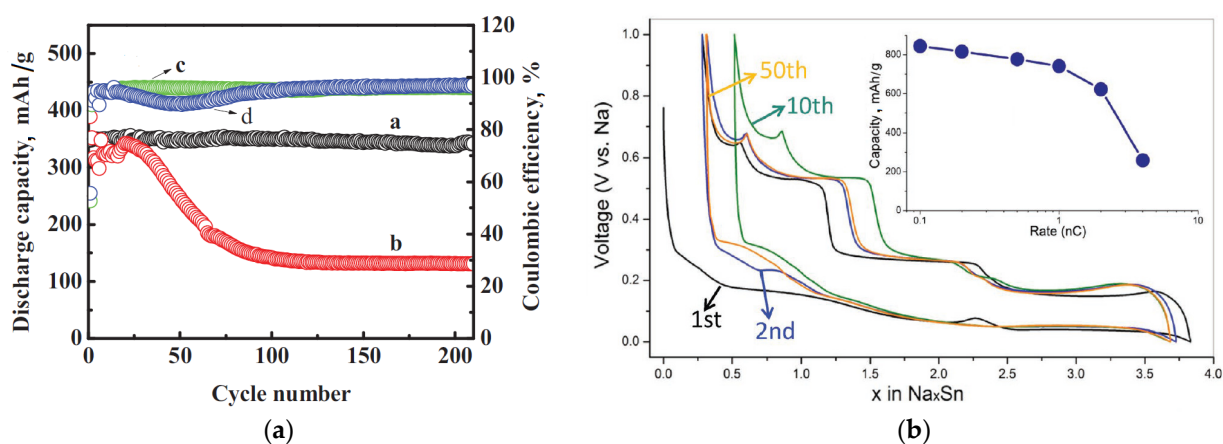


Figure 8. (a) Cycling performance (a, b) and Coulombic efficiency (c, d) at a cycling rate of 0.2 C in FEC-containing (a, c) and FEC-free (b, d) NaPF₆/EC/DEC electrolytes NaPF₆/EC/DEC electrolyte of porous CNF-SnSb electrodes. (Reprinted with permission from [151]. Copyright 2014, Wiley Online Library). (b) Performance of Sn electrode in 1 M NaPF₆/DGME electrolyte: voltage profiles with their rate capability (inset), where 1 C equal to 847 mA/g. (Reprinted with permission from [165]. Copyright 2016, Wiley Online Library).

The features of SEI on bismuth have been studied mainly on samples of various composites of bismuth with carbon. In [169], a composite obtained by carbonization of bismuth citrate and containing 83% bismuth was studied. It is also shown here that loose SEIs with a thickness of about 15 nm containing ester polymerization products are formed in the carbonate electrolyte. Dense SEIs about 3 nm thick was deposited in an electrolyte based on ethylene glycol dimethyl ether. Similar results were obtained in [172,173]. The authors of [170] describe a composite in which bismuth nanospheres are encapsulated in porous carbon doped with nitrogen. On such a composite in 1 M NaPF₆ in DME, stable SEIs are realized, which ensure the reversible sodium insertion at currents up to 100 A/g. However, without some special measures, such electrodes demonstrate rather high irreversible capacity at the first cycle (Figure 9a). Almost the same material is described in [175]. A peculiar composite of bismuth with carbon is described in [171,174]. Here, bismuth nanorods are enclosed in carbon nanotubes doped with nitrogen. On such a composite, SEIs at cathodic polarization appeared at potentials of about 0.64 V (which was noted by a rather narrow peak in the voltammogram) and ensured stable cycling (2600 cycles at a current of 1 A/g). In [176], copper was used as a model material for studying the mechanical properties of SEIs formed in 1 M NaPF₆ in an EC–DEC mixture. It is unclear, however, to what extent the conclusions of this work can be extended to other substrates and other electrolytes.

It is known that sodium (unlike lithium) practically does not insert into crystalline silicon [267,268]. However, there are indications of the possibility of reversible insertion of sodium into amorphous silicon [178] from an electrolyte based on an EC-PC mixture with the consumption of a noticeable irreversible capacity for the formation of SEI at potentials about 1.1 V (Figure 9b). In [177], the process of sodium insertion into clathrate (openwork) structures of type II silicon (type II clathrates have the formula Na_xSi₁₃₆, where 0 < x < 24), and it was found that in this case, the formation potential and some properties of SEI depend on temperature, since side processes are accelerated with increasing temperature, leading to irreversible capacity.

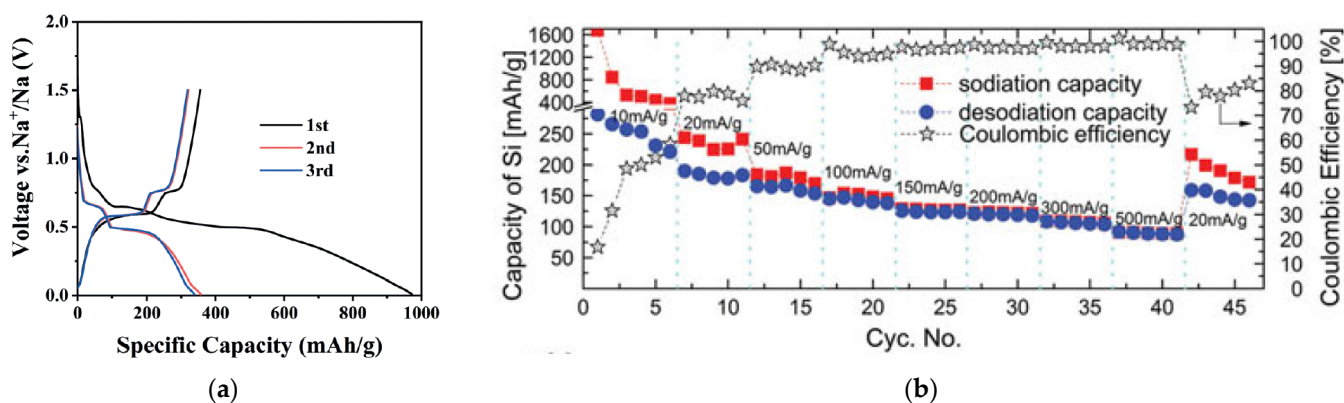


Figure 9. (a) Galvanostatic charge/discharge curves of Bi@N-C for first three cycles at 1 A/g. (Reprinted with permission from [170]. Copyright 2019, Wiley Online Library). (b) Rate capability at different current rates of Si NP electrodes. (Reprinted with permission from [178]. Copyright 2016, Wiley Online Library).

The closest analog of silicon, germanium, on the contrary, is capable of reversible sodium incorporation [179]. In this case, side processes of electrolyte reduction also occur, accompanied by irreversible capacity, but we are unaware of research on the composition and structure of the resulting SEI. It is worth mentioning that the irreversible capacity of germanium (in contrast to carbon materials) is noticeably reduced by the addition of VC [180]. The effect of VC is vividly shown in Figure 10.

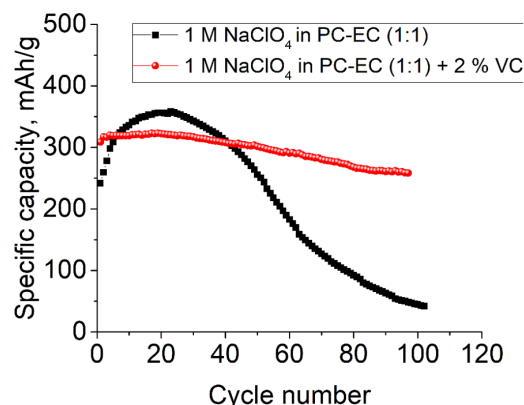


Figure 10. Change in the discharge capacity of Ge nanorods at galvanostatic cycling with a current density of 125 mA/g in VC-free electrolyte (black squares) and electrolyte with 2% VC (red circles). (Reprinted with permission from [180]. Copyright 2022, MDPI, Open Access).

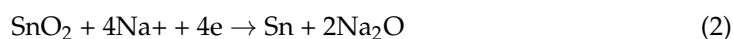
Many oxides, including Fe_3O_4 , are used as anode materials in the form of composites with carbon or in the form of carbon-coated nanoparticles. One can venture a guess that it is the presence of carbon components that determines the nature of SEI on such materials. In [181], on an electrode of Fe_3O_4 nanoparticles with a thin carbon coating in an electrolyte consisting of 1 M NaClO_4 in ethyl methanesulfonate with the addition of FEC, the formation of SEI was recorded at potentials of about 1.3 V. In [188], Fe_3O_4 nanorods with a thin carbon coating in an electrolyte, consisting of 1 M NaClO_4 in the usual EC:PC mixture were studied, and the formation of SEI was found only at potentials of about 0.4 V. This difference is undoubtedly due to the difference in the nature of the electrolyte. In [190], as well as in [189,191], nanostructured Fe_2O_3 electrodes without carbon coating on individual particles are described (however, using 20% carbon black as an electrically conductive additive in the active mass of electrodes). On such electrodes in 1 M NaClO_4 in an EC:DEC mixture, the formation of SEI occurred in the potentials about 0.4 V, i.e., in the same way as on Fe_3O_4 nanorods with a carbon coating.

Titania is one of the popular candidates for the negative electrode material of sodium-ion batteries. As a rule, it is used in the modification of anatase, and both carbon-coated and uncoated materials are described. Already in the first publications [196–198], the existence of an appreciable irreversible capacitance on such electrodes associated with the formation of SEI was noted. In [196], the irreversible capacity appeared only in the first cycle, while in [197,198], it gradually decreased from the first to the tenth cycle. As a rule, in solutions based on an EC:PC mixture, SEIs are formed at potentials of 1.1–1.2 V [199,200], although in [196], a potential of about 0.8 V is indicated, and in [201], about 0.4 V for NaClO₄ solution in pure PC. In [200], the influence of the nature of the electrolyte on the formation of SEI was studied in more detail, and the effect of the solvent was shown to be stronger than that of the salt anion. Thus, in a solution of NaTFSI in PC, the irreversible capacity in the first 10–15 cycles were significantly greater than in solutions of NaPF₆ and NaClO₄ in the same solvent. For NaClO₄ solutions, the irreversible capacity decreased in the series of solvents (EC:DMC)-PC-(EC:PC). In the same work, the practical absence of the effect of the addition of 2% FEC on the electrochemical behavior of TiO₂ in 1 M NaClO₄ solutions in an EC:PC mixture was noted (which contradicts the results of many other studies, for example, [205]). The works [192,202] show the effect of pre-sodiation of electrodes based on TiO₂ on the reduction in the irreversible capacity.

An original approach for reducing the irreversible capacitance on titania-based electrodes is described in [185]. Here, an array of anatase nanotubes is proposed to be preliminarily lithiated in a LiClO₄ solution in PC, and then Li-containing SEIs are converted into Na-containing SEIs in a NaClO₄ solution.

Tin oxides and their composites with carbon have also been considered promising materials for the negative electrodes of sodium-ion batteries. The processes of SEI formation on such materials were studied in [219–228]. It was found in [219] that the composition of SEI on the SnO₂-reduced graphene oxide composite formed in an electrolyte based on EC:DEC with the addition of FEC includes NaF, Na₂CO₃, and sodium alkyl carbonates. On a SnO₂ composite with multiwalled carbon nanotubes in a NaClO₄ solution in EC:PC, SEI was formed at potentials in the range from 0.5 to 0.2 V [220]. A somewhat unusual composition of SEI on the SnO₂ nanocomposite with carbon Super P is presented in [228]. Here, in a 1 M solution of NaClO₄ in an EC:DEC mixture with the addition of FEC, SEIs were formed containing, in addition to the usual sodium fluoride, carbonate, and alkyl carbonates, also sodium chloride, and chlorate. In [262], the behavior of electrodes made of a SnO₂ composite with graphene in an electrolyte based on an ionic liquid (1 M NaFSI in PMP:FSI) was studied, and a cathode peak was recorded on voltammograms at potentials of about 0.6 V, associated with the formation of SEI, which turned out to be thinner and more homogeneous than the SEI formed in the PC-EC electrolyte.

When analyzing the processes of sodium insertion into materials based on oxides, it should be taken into account that, in these cases, there are at least two mechanisms for the appearance of the irreversible capacity of the initial cycles. First, these are the processes of reduction in electrolyte components, leading, in particular, to the formation of SEI. Secondly, these are the processes of reduction in oxides themselves. For example, for electrodes based on SnO₂, during the first charge at potentials of 3–0.8 V, sodium ions are introduced into the structure of tin dioxide. At potentials more negative than 0.8 V, the sodium ion interacts with tin dioxide to form tin and Na₂O nanoparticles. Finally, at potentials more negative than 0.1 V, the formation of the Na_xSn alloy is observed. The authors of [269] have shown that during the electrochemical reduction in thin layers of highly porous SnO₂ on a copper substrate, firstly, Na₂O and tin are formed according to the equation, and then a series of intermetallic compounds NaSn₃, α-NaSn, Na₉Sn₄ and Na₁₅Sn₄ appear. During the discharge process, the latter again turns into the tin. The same remark applies to the insertion of sodium into materials based on chalcogenides.



Among other oxide materials on which SEI formation processes were studied, mention should be made of oxides of cobalt [186,207–212], antimony [214–217], niobium [218], and nickel [184,213]. According to the data of [214], SEI on Sb_2O_4 in an electrolyte based on EC-DMC are formed at potentials of about 0.43 V. The authors of [215] report that on a SbO_x composite with reduced graphene oxide in an EC-PC-based electrolyte, SEI at the first cycle is formed at potentials of about 0.46 V.

Of the chalcogenides proposed as active anode materials in sodium-ion batteries, sulfides (FeS [230], Fe_3S_4 [237], Bi_2S_3 [229], MoS_2 [231,241], WS_2 [234], SnS_2 [235,243], Sb_2S_3 [242], Ni_3S_2 [236]) and selenides (SnSe_2 [232], CoSe [238], ZnSe [239], $\text{MoSe}_{0.85}\text{S}_{0.15}$ [240], FeSe_2 [270]) arouse keen interest.

The work [229] confirmed the sodium insertion mechanism described above, including the stage of bismuth sulfide reduction with the formation of bismuth metal and Na_2S . This work and [231] also confirmed the trivial conclusion that on electrodes based on Bi_2S_3 nanorods in an electrolyte based on EC:DEC loose unstable SEIs are formed, which are the main reason for capacity fading, while thin dense SEIs are obtained in a DME-based electrolyte (Figure 11a). In addition, the cycling of Bi_2S_3 nanorods in a DME-based electrolyte was found to result in surface coarsening, which increases the irreversible capacity. Doping Bi_2S_3 with iron and depositing a thin carbon coating on the nanorods prevent etching and radically change the character of SEIs, enriching them with sodium fluoride and reducing their impedance.

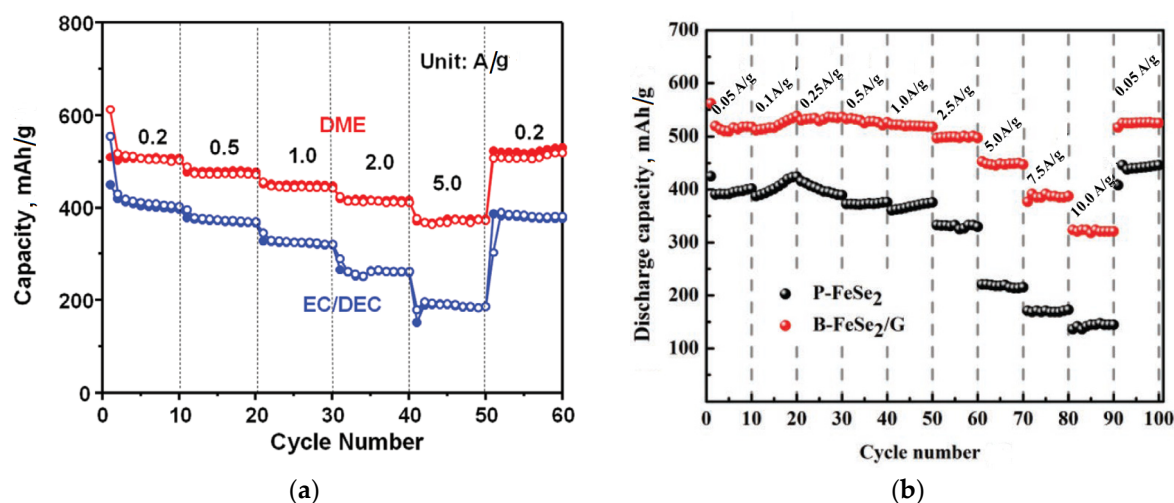


Figure 11. (a) Rate performance of $\text{MoS}_2@\text{C}$ in DME and EC/DEC electrolytes. (Reprinted with permission from [231]. Copyright 2020, Wiley Online Library). (b) The rate capability of P-FeSe_2 and $\text{B-FeSe}_2/\text{G}$ at various current densities. (Reprinted with permission from [270]. Copyright 2019, Wiley Online Library).

In [230], an unusual binder, specifically sodium polyacrylate, was used for FeS -based electrodes. In this case, in a solution of 1 M NaCF_3SO_3 in diethylene glycol dimethyl ether as an electrolyte, ductile SEIs were formed at potentials of about 0.8 V. Some amounts of sodium polyacrylate were found in the organic components of SEI, and here the organic components were localized in surface layers of the SEI, and mineral ones in the inner layers, too.

The example of chalcogenide-based electrodes shows the influence of the structure of electrodes on the properties of SEI. For instance, composite electrodes with a sandwich-like structure consisting of SnSe_2 and reduced graphene oxide layers were studied in [232], with the content of reduced graphene oxide being as low as 7.3%. According to the authors, it was this electrode structure that ensured the formation of thin reliable SEIs as a result of the abundance of Sn-O-C bonds. It was shown in [233] that for Sb_2Te_3 composites with carbon nanotubes, the thickness and continuity of the SEI depend on the ratio of these components, and, in the optimal case (10% carbon nanotubes), the thickness of the SEI

formed in 1 M EC:PC with the addition of FEC is 19 nm. For plain Sb_2Te_3 (without carbon nanotubes), the SEI thickness was 67 nm. [234] states that it is the thin carbon coating on the tungsten disulfide particles that ensures the formation of thin, high-quality SEIs. The original globule-like FeSe_2 /graphene structure (B- FeSe_2 /G) is described in [270]. Here graphene layers wrap the surfaces of FeSe_2 particles and stretch into the interior of these particles. Such structures display higher electrochemical performance than particulate P- FeSe_2 (Figure 11b).

An interesting example of the use of tin sulfides is the work [139]. Here, the active material of the negative electrode is activated carbon, on the surface of which particles the thinnest layer of SnS and SnS_2 nanosheets, which play the role of an artificial SEI, are deposited.

In [263], data are presented on the formation of reliable SEIs on electrodes made of Sb_2S_3 composite with graphene in an electrolyte based on an ionic liquid (1 M NaFSI in PMP:FSI).

Phosphorus and some phosphides are promising materials for the negative electrode of sodium-ion batteries [271]. As a rule, phosphorus is used as composites with various forms of carbon. SEIs are also formed on such electrodes during cathodic polarization, and the mechanism of this process does not have any specific features; however, the properties of SEIs depend on the composition of the composite, i.e., from the ratio P:C [247]. In [250], a “core-shell” structure was proposed, where the core was composed of a composite of red phosphorus with ball-milled carbon nanotubes, and the shell was a thin (less than 10 nm) polydopamine film playing the role of SEI. In [249], it is proposed to deposit a thin coating of amorphous TiO_2 on particles of a red phosphorus composite with milled carbon nanotubes. The presence of such a coating, according to the authors, provides the formation of thin continuous ductile SEI enriched with NaF and has a reduced resistance. In [251], it is proposed to apply a thin coating of nickel to red phosphorus particles.

Of the phosphides proposed as negative electrodes, the most popular are Sn_4P_3 [244,245,272], as well as VP_2 [248], CoSi_3P_3 , and FeSi_4P_4 [246]. It was shown in [244] that the combined addition of FEC + TMSP provides the same reliable SEI on the surface of the phosphide as on the surface of hard carbon. In [248], high-quality SEIs were obtained on a VP_2 electrode in an ionic liquid-based electrolyte.

The properties of SEIs formed on such negative electrodes as sodium titanate have been studied in [252–255,273]. In addition, information is provided on SEI on $\text{Na}_3(\text{TiOPO}_4)_2\text{F}$ [256], NaTiOPO_4 [182], ZnSnO_3 composite with carbon [257], Bi_2MoO_6 [259], and CuCrP_2S_6 [260].

5. CEI on Cathode Materials

Passive films on the materials of positive electrodes of sodium-ion batteries have been studied much less than SEI on negative electrodes. Moreover, since a wide variety of materials have been proposed as functional cathode materials, the characteristics of CEI on each specific material have been studied at best in one or two papers. The very existence of passive films as products of electrolyte oxidation was confirmed by direct electron microscopic studies in [274] for $\text{Na}_{0.70}\text{Mn}_{0.80}\text{Co}_{0.15}\text{Zr}_{0.05}\text{O}_2$ (it is noted that it was zirconium doping that ensured the formation of dense thin CEI), in [275] for $(\text{Ni}_{0.4}\text{Co}_{0.4}\text{Mn}_{0.2})_3\text{O}_4$ and in [276] for $\text{Na}_{0.67}\text{Mn}_{0.625}\text{Fe}_{0.25}\text{Ni}_{0.125}\text{O}_2$.

In [277], reliable conclusions about the properties of CEIs formed on $\text{Na}_2\text{Fe}_x\text{Fe}_{1-x}(\text{SO}_4)_2(\text{OH})_x$ during the first anodic polarization in 1 M NaClO_4 in an EC:DMC:EMC mixture were made based on the results of electrochemical impedance spectroscopy. In an equivalent circuit, CEI is described by a parallel combination of a constant phase element Q_{CEI} and resistance R_{CEI} . The last element depends on the potential and, at potentials from 1.5 to 3.9 V, is approximately 1.5 Ohm (for a particular cell), and as the potential increases to 4.5 V, it increases almost linearly to 7 Ohm as a result of an increase in the CEI thickness.

It was shown in [278] that stable, reliable CEIs are formed on $\text{NaNi}_{0.68}\text{Mn}_{0.22}\text{Co}_{0.1}\text{O}_2$ in an electrolyte consisting of 1.5 M NaFSI in a mixture of DEC with tris (2,2,2-trifluoroethyl)

phosphate (TFP). We deem it possible to assume that the stability of such CEIs is determined by the optimum solvating capacity of said solvent.

Like SEI, the properties of CEI depend on the presence of an FEC additive in the electrolyte. According to [279], the addition of FEC to a solution of NaClO₄ in PC inhibits the oxidation of PC on the surface of NaCo_{0.7}Mn_{0.3}O₂ and promotes the formation of CEI enriched in NaF.

The authors of [280] found that the behavior of Prussian blue cathodes depends on the content of uncoordinated water molecules (so-called zeolite water). The content of zeolite water, in turn, depends on the Prussian blue synthesis temperature, the optimal temperature being 80 °C. CEI enriched with Na₂CO₃ are deposited on the material synthesized in this mode, which ensures stable cycling of the positive electrodes.

It was shown in [281,282] that the addition of ionic liquids to PC-based electrolytes leads to a noticeable improvement in CEI on Na₃V₂(PO₄)₃–carbon composites.

6. Conclusions

Characteristics of sodium-ion batteries largely depend on the presence and properties of passive films formed on the surface of active materials of negative and positive electrodes. Passive films on negative electrodes result from the reduction in electrolyte components (solvent and salt anion). They have the properties of a solid electrolyte with sodium ion conductivity and are insulators in terms of electronic conductivity. Their thickness is a few (or dozen) nanometers. Usually, they are called SEI—solid electrolyte interphase. The formation of SEI is associated with the consumption of a certain charge, which is an irreversible capacity. Passive films on the surface of positive electrodes (CEI—cathode electrolyte interphase) arise as a result of electrolyte oxidation.

The formation process and properties of SEI depend both on the nature of the electrode material and on the nature of the electrolyte and the conditions for its reduction (including temperature, current density, etc.). In some cases, thin dense SEIs of uniform thickness with high ionic conductivity are formed, which provide long-term efficient cycling of negative electrodes with low-capacity fading. In other cases, SEIs are thick, unevenly distributed over the surface, and have high Ohmic resistance, resulting in poor cyclability. In many cases, electrolyte additives have a beneficial effect on SEI properties. The most effective and popular additive is fluoroethylene carbonate. The most studied are SEI on electrodes based on hard carbon, other carbon materials, some metals, oxides, chalcogenides, and phosphides. In Table 1, some information on SEI composition on various electrodes in various electrolytes, as well as on irreversible capacity at initial cycles, is summarized.

Table 1. SEI composition and irreversible capacity at the first cycle.

Electrode Material	Electrolyte	SEI Composition	Q _c /Q _a 1st Cycle	Ref.
HC	1 M NaClO ₄ in EC:DEC (3:7)	-	350/300	[60]
HC	1 M NaPF ₆ in DEC:EC (1:1)	NaF, Na ₂ CO ₃ , Na _x PF _y , ROCO ₂ Na	-	[69]
	1 M NaClO ₄ in DEC:EC (1:1)	NaCl, Na ₂ CO ₃ , Na _x PF _y , ROCO ₂ Na, PEO	-	
	1 M NaTFSI in DEC:EC (1:1)	NaF, ROCO ₃ Na, ROna, PEO	-	
	1 M NaTFSI in DEC:EC (1:1)	NaF, ROCO ₃ Na, ROna, PEO	-	
	1 M NaFSI in DEC:EC (1:1)	NaF, Na ₂ SO ₄ , Na ₂ S, ROCO ₃ Na, ROna, PEO	-	
HC	1 M NaPF ₆ in EC:DMC (1:1) + 3% FEC	NaF, Na ₂ CO ₃ , R-COONa, NaO ₂ CO-C ₂ H ₄ -OCO ₂ Na	320/220	[70]
	1 M NaTFSI in EC:DMC (1:1) +3% FEC	Na ₂ CO ₃ , NaF, NaO ₂ CO-C ₂ H ₄ -OCO ₂ Na	275/175	

Table 1. Cont.

Electrode Material	Electrolyte	SEI Composition	Q _c /Q _a 1st Cycle	Ref.
HC	0.5 M NaBPh ₄ in DME	NaF	275/261	[71]
	0.5 M NaPF ₆ in DME	NaF	276/261	
	0.5 M NaFSA in DME	Na ₂ S	270/244	
	0.5 M NaTFSA in DME	NaF	234/207	
	1 M NaPF ₆ in EC:DEC (1:1)	NaF	271/251	
HC	1M NaClO ₄ PC:EC (1:1)	Na ₂ CO ₃ , (CH ₂ OCO ₂ Na) ₂ , Na ₂ CO ₃ , R-OCO ₂ Na	275/190	[74]
	1 M NaBF ₄ in tetraglyme	R-ONa, -C-O-C-, CH ₃ OCH ₂ CH ₂ O-, O-CH ₂ -	320/278	
HC	1 M NaODFB in DME	RCH ₂ ONa; groups C=O/B-O, groups B-F; B-O, Na ₂ CO ₃	290/175	[75]
	1 M NaPF ₆ in DME	NaF; Na ₂ CO ₃ ; RCH ₂ ONa	265/250	
HC	1 M NaClO ₄ in EC:PC:DMC (0.45:0.45:0.1)	Na ₂ CO ₃ , ROCO ₂ Na, R-CH ₂ -OCO ₂ Na, PEO	560/360	[77,79]
HC	1 M NaTFSI in PC + 3% FEC	Na ₂ CO ₃ , NaF, sodium organic salts	570/220	[78]
HC	1M NaClO ₄ in EC:PC (1:1) + 5% FEC	PEO; Na ₂ CO ₃ ; NaF; groups C-F	910/301	[80]
	1M NaClO ₄ in TEGDME	Sodium alkoxides; Na ₂ CO ₃ ; Na ₂ CH ₂ R	1050/363	
HC	1 M NaPF ₆ in PC + 0.5% FEC	Na ₂ CO ₃ , NaF, Na-O-(C=O)-O-CH ₂ -R, Na-O-(C=O)-O-R, Na ₂ CO ₃ , NaF	280/240	
	1 M NaPF ₆ in PC:EC + 0.5% FEC	Na-O-(C=O)-O-CH ₂ -R, Na-O-(C=O)-O-R, Na _x PF _y , Na _x PO _y F _z	280/240	
HC	1 M NaPF ₆ in DME + 0.5% VC	Na ₂ CO ₃ , RCO ₂ Na, NaF, -OCO ₂ CH=CH) _n -	210/200	
	1 M NaPF ₆ in DEGDME + 0.5% VC			
HC	1 M NaClO ₄ in EC:DEC (1:1)	Na ₂ CO ₃ , RNa, ROCO ₂ Na, (CH ₂ -CH ₂ -O-) _n	400/325	[101]
HC	1 M NaPF ₆ in EC:DEC (1:2)	NaF, Na ₂ CO ₃ , Na _x PF _y O _z	335/235	[109]
Graphite	1 M NaPF ₆ in EC:DEC (1:1)	CH ₃ CH ₂ OCO ₂ Na, (CH ₂ OCO ₂ Na) ₂ , Na ₂ CO ₃ , NaF	120/30	[120]
	1 M NaPF ₆ in diglyme	CH ₃ OCH ₂ CH ₂ ONa, CH ₃ CH ₂ OCH ₂ CH ₂ ONa, Na ₂ CO ₃ , NaF	260/160	
Sb	1 M NaClO ₄ in PC	Na ₂ CO ₃ , NaF, alkylcarbonates	714/550	[146]
	1 M NaPF ₆ in EC:DMC	Na ₂ CO ₃ , NaF, alkylcarbonates	740/620	
	1 M NaPF ₆ in PC + 5% FEC	Na ₂ CO ₃ , NaF, alkylcarbonates	735/580	
Sn ₄ P ₃	1 M NaClO ₄ in EC:PC (1:1) + 5% FEC	Na ₂ CO ₃ , NaF	720/560	[244]
	1 M NaClO ₄ in EC:PC (1:1) + 5% FEC + 0.5% in TMSP	Na ₂ CO ₃ , NaF, SiF	880/680	
Na ₂ Ti ₃ O ₇	1 M NaClO ₄ in EC:PC (1:1)	Na ₂ CO ₃ , NaCO ₃ R, NaF, NaCl, NaOR, PEO, poly(ethylene oxide)s	385/170	[252]
FeS	1 M NaCF ₃ SO ₃ in diglyme	Na ₂ CO ₃ , Na ₂ CO ₂ R, NaF	600/500	[230]
MoS ₂ @C	1 M NaPF ₆ in EC:DEC (1:1)	RONa, Na ₂ CO ₃ , ROCOONa, RCH ₂ ONa	500/450	[231]
Na ₂ Ti ₃ O ₇	1 NaClO ₄ in EC:PC + 1 % FEC	NaF, Na ₂ O, Na ₂ CO ₃ , NaHCO ₃ , ROCO ₂ Na	250/200	[253]

Table 1. Cont.

Electrode Material	Electrolyte	SEI Composition	Q _c /Q _a 1st Cycle	Ref.
SnSe ₂	1 M LiPF ₆ in EC:DMC (1: 1)	NaF, Na ₂ CO ₃ , polyethers, Se-O	750/525	[235]
TiO ₂	1 M NaClO ₄ in EC:PC (1:1)	Na ₂ CO ₃ , ROCO ₂ Na	-/200	[185]
Ni ₃ S ₂ @NS-CNTs	1.0 M NaSO ₃ CF ₃ in diglyme	NaF, Na ₂ CO ₃ , Na ₂ SO ₃ , organic polyethers, C-F _x components	470/435	[236]
TiO ₂	1 M NaPF ₆ EC:DEC (1:1) + 3% VC	Polycarbonates, Alkyl carbonates	350/160	[187]
	1 M NaPF ₆ in diglyme	Polyethers	320/150	
Fe ₃ S ₄	1.0 M NaClO ₄ in DMC:EC (1:1)	RCH ₂ ONa, Na ₂ CO ₃ , NaOH	600/530	[237]
NaTiOPO ₄	1 M NaClO ₄ in EC:PC (1:1)	Hydrocarbons, alkyl-carbonates, carbonates, NaF, ethers	110/80	[258]
Li ₄ Ti ₅ O ₁₂	1 M NaPF ₆ in diglyme	RCH ₂ ONa, ROCO ₃ Na, NaF, Na ₂ CO ₃ , R-CO ₃	300/160	[254]
	1 M NaPF ₆ in EC:DMC (3:7)	NaF, CF _x , Li ₂ CO ₃	275/140	
Sn	1 M NaPF ₆ in diglyme	RCH ₂ ONa, Na ₂ CO ₃ , NaOH, Na ₂ O, NaF	850/780	[165]
Sn films	1 M NaClO ₄ in PC	Na ₂ CO ₃ , NaCl	900/800	[166]
Graphite	1 M NaFSI in TEGDME	NaF, polyethers	160/110	[141]
Fe ₂ O ₃	NaClO ₄ in EC:DEC (2:1)	NaOH, Na ₂ CO ₃ , alkyl carbonates ROCO ₂ Li	-	[189]
Sb	1 M NaClO ₄ in PC + 5% FEC	NaOH, Na ₂ O, NaF, NaCl	770/600	[157]
rGO	1 M sodium triflate (NaOTf) in (EC-DEC (1:1))	Na ₂ CO ₃ , Na ₂ CO ₂ R, polyesters, RSO ₃ Na, NaF	1200/500	[143]
	1 M sodium triflate (NaOTf) in diglym	CF ₃ , Na ₂ CO ₃ , Na ₂ CO ₂ R, polyesters, RSO ₃ Na, NaF	700/650	
Bi	1M NaPF ₆ in diglyme	R-COO-Na, RCH ₂ ONa, Na ₂ CO ₃ , sodium alkylcarbonates, polyesters	420/400	[261]
meso-porous Co ₃ O ₄	1 M NaPF ₆ in EC:DEC + 5% FEC	R-CH ₂ -OCO ₂ Na, R-CH ₂ -OCO ₂ Na, Na ₂ CO ₃ , NaOH, NaF	790/750	[212]
	1 M NaPF ₆ in FEC:DEC	R-CH ₂ -OCO ₂ Na, R-CH ₂ -OCO ₂ Na, Na ₂ CO ₃ , NaOH, NaF	820/750	
Na ₃ V ₂ (PO ₄) ₃	0.25 M NaPF ₆ -incorporated in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (BMITFSI IL)	NaF, NaOH, Na ₂ SO ₄ , Na ₂ S ₂ O ₇	108/135	[282]

The analysis of Table 1 shows that SEI principal composition on various electrodes is, by and large, almost the same. The main variations in SEI composition, e.g., the presence of Na₂SO₄, Na₂S, and SiF, are associated with features of special electrolytes. It is clear that the composition of inorganic components of SEIs is determined by the nature of the salt's anion, whereas the composition of organic components is associated mainly with the nature of solvents.

CEI studies are few and far between. However, the very existence of CEI has been proven by electron microscopy studies, and the beneficial effect of fluoroethylene carbonate additives on the characteristics of CEI has also been confirmed.

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Abbreviations

SEI	solid electrolyte interphase
CEI	cathode electrolyte interphase
EC	ethylene carbonate
PC	propylene carbonate
DEC	diethyl carbonate
DMC	dimethyl carbonate
RCH ₂ ONa, RNa	sodium alkoxides
NaFSI	sodium bisfluorosulfonylimide
DME	1,2-dimethoxyethane
BTFE	bis(2,2,2-trifluoroethyl) ether
FEC	fluoroethylene carbonate
PVdF–HFP	polyvinylidene fluoride with hexafluoropropylene
Q _{rev}	reversible capacity
Q _{irr}	irreversible capacity
NaTFSI	sodium bis(trifluoromethanesulfonyl)imide
NaFTFSI	sodium fluorosulfonyl-(trifluoromethanesulfonyl)imide
XPS	photoelectron spectroscopy
ROCO ₃ Na	sodium alkyl carbonates
VC	vinylene carbonate
DFT	density functional theory
TMSP	tris(trimethylsilyl)phosphite
NaODFB	sodium-difluoro(oxalate)borate
ROSO ₂ Na	sodium alkyl sulfates
RSO ₃ Na	sodium alkyl and sulfites
DEGDME	diethylene glycol dimethyl ether, diglyme
TEGDME	tetraethylene glycol dimethyl ether
PMP–FSI	N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide
PMP-TFSI	N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
TFP	tris (2,2,2-trifluoroethyl) phosphate

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