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Mini review

A Brief Review of Post-Lithium-Ion Batteries

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Energy storage is an extremely important problem today. Among the most efficient batteries, lithium-ion occupy a special place. Lithium is the most active known reducing agent. It has a huge energy storage resource. 1 kg of lithium is capable of storing 3860 ampere-hours. However, lithium-ion batteries have almost reached their limits and are characterized by a high cost, which raises the question of the further development of such technologies based on the so-called post-lithium-ion batteries. This paper provides an overview of post-lithium-ion batteries such as lithium-oxygen batteries, sodium-ion batteries, lithium-sulfur batteries and their comparison with known lithium-ion batteries. The commercialization of post-lithium-ion batteries is also discussed.

Keywords: Lithium-ion batteries; Lithium-oxygen batteries; Sodium-ion batteries; Lithium-sulfur batteries; Post-lithium-ion batteries

1. INTRODUCTION

Renewable energy sources, including wind and solar energy, play a key role in the decarbonization of the energy system of the whole world. According to the World Energy Council, the total capacity of wind turbines around the world by 2020 will be 474 GW. Electricity received from photovoltaic modules should reach 100 GW by 2020 [1].

However, it is now obvious that in order to smooth out the unregularly production of renewable energy, highly efficient and low-cost energy storage devices are needed.

For such systems, the rate of energy storage and long service life (number of cycles), as well as the relatively low cost, are extremely important. There is an opinion [1], that in order to be competitive, the capital costs of storage technologies for energy applications must be comparable or lower than $ 250/kWh, provided that the life cycle is 15 years or 3900 cycles. Capital cost of $ 1,250/kW or less is desirable. To some extent, the electrochemical technologies satisfying these requirements could be divided into two main groups: batteries and hydrogen technologies based on electrolyzers and fuel cells [2]. Currently, lithium-ion batteries are beginning to dominate in the field of relatively short-term energy storage.

The importance of the lithium-ion technology is so great that in 2019, John B. Goodenough, M. Stanley Whittingham and Akira Yoshino won the Nobel Prize in Chemistry for the invention of the first prototype of a lithium-ion battery with a positive electrode made of $LiCoO_2$ and a negative electrode made of graphite [3].

Lithium-ion batteries operate with a voltage of about 3.7 V and exhibit an energy density of about 220 Wh/kg [4]. The last research and development have allowed to reduce significantly the cost and to increase the safety of lithium-ion batteries, in particular, to solve the problem associated with dendrite formation on the electrodes because of charge-discharge cycles and the subsequent short circuit of the electrodes. It is worth noting the lithium iron phosphate cathode batteries (LFP batteries), which are one of the safest types of lithium-ion batteries. The specific capacity of lithium iron phosphate (170 mAh/g) is higher than the specific capacity of lithium manganese spinel (145 mAh/g) or lithium cobaltate (140 mAh/g). However, the relatively low voltage of $LiFePO_4$ (~ 3.45 V) leads to a lower specific energy of LFP batteries [5-10]. During cycling, $LiFePO_4$ is very stable.

It should also be noted the development of electrodes based on lithium titanate $Li_4Ti_5O_{12}$, which are recognized as safe electrodes for the replacement of graphite anodes [11, 12]. The development of various layered compounds, such as $LiNiO_2$, $LiNi_xCo_yO_2$, $LiMn_xCo_yO_2$, $LiMn_xNi_yO_2$, $LiNi_xCo_yAl_zO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, etc., as a cathode that can reduce the cost of the batteries and make the cathode more stable [13-15]. The development of high-voltage cathodes based on spinel-type $LiMn_2O_4$ and its derivatives, which provide a discharge potential of more than 4.0 V and a specific capacity of 147 mAh/g with a good cycling. However, LMNO-type spinel exhibits the capacity about 10% less than that of $LiCoO_2$ and a significant loss of capacity at elevated temperatures [13-15].

Much attention was paid to safety and reliability.

Measurements of the entropy changes of individual electrodes ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, graphite, $Li_4Ti_5O_{12}$) showed that some cathode / anode pairs, for example, $LiFePO_4$ (cathode) and $Li_4Ti_5O_{12}$ (anode), can reduce the rate of the heat release and a battery overheating due to compensation of the total heat evolution [16, 17].

A significant progress was reached in the increasing the battery life-time (number of cycles). Recently, it was announced the achievement of 20,000 charging cycles (~ 50 years) at a current of 5 C for an 18650 battery with $LiFePO_4/Li_4Ti_5O_{12}$ electrodes [18]. Based on such batteries high power storage systems are implemented [19].

So, against the background of a rapid development of renewable energy sources, storage technology based on lithium-ion batteries now already allows maintaining the stability of the electricity systems and could be used for a quickly response to frequency fluctuations in the network. However, lithium-ion batteries have almost reached their limits and are still characterized by high cost, which raises the question of the further development of similar technologies based on the so-called post-lithium-ion batteries.

2. POST-LITHIUM-ION BATTERIES

The term "post-lithium-ion batteries" refers to electrochemical systems whose specific energy is significantly higher than the specific energy of modern lithium-ion batteries. Post-lithium-ion systems also include battery systems, whose specific energy is comparable to the specific energy of modern commercial lithium-ion batteries, but their projected cost will be significantly lower or other key characteristics will be significantly higher. Currently, lithium-oxygen batteries, sodium-ion batteries and lithium-sulfur batteries are referred to post-lithium-ion systems. None of these systems is ready for industrial production today, but active research is underway for each of these systems.

2.1. Lithium-Oxygen Batteries

The first mention of a lithium-oxygen battery refers to 1996, when K. M. Abraham and Z. Jiang published an article “A Polymer Electrolyte-Based Rechargeable lithium / Oxygen Battery” in the journal of the J. Electrochemical Society, proposing a reversible reaction mechanism on a positive electrode and confirmed this mechanism using electrochemical and physicochemical research methods [20].

In general, a lithium-oxygen battery consists of a lithium negative electrode, a porous carbon cathode and an electrolyte. Different electrolytes are used: a liquid aprotic electrolyte (in this case, the electrodes are separated by a conventional separator), an aqueous electrolyte (in this case, the lithium electrode is protected by a solid electrolyte) and a polymer electrolyte (in this case, the use of a separator is not required) (Fig. 1). When such a battery is discharged, a reversible lithium dissolution / precipitation reaction takes place on the negative electrode, while oxygen reduction / oxidation of the reaction products occurs on the positive electrode.

The total cell reaction is:

$Li + 1/2O_2 \rightarrow 1/2Li_2O_2$ – when the battery is discharged (1)

$1/2Li_2O_2 \rightarrow Li + 1/2O_2$ – when the battery is charged (2)

The discharge voltage of a lithium-oxygen battery is only about 2.5 V, but due to the high theoretical specific capacity of lithium and oxygen, the specific energy of the lithium-oxygen battery is about 3000 Wh/kg, which is 6 times higher than the corresponding value for a lithium-ion battery, for example, for a system lithium cobaltate - graphite.

The main problems encountered in the development of lithium-oxygen batteries are the selection of an electrolyte, the synthesis of catalysts to reduce the overvoltage of lithium peroxide decomposition, the study of traces of water influence on the formation of solid reaction products, and the study of a porous cathode passivation by reaction products.

It was found that that the oxygen reduction reaction can proceed by two mechanisms: in two stages with the formation of intermediate products (superoxide particles) and then with the reduction of lithium peroxide or in one stage, a one-stage two-electron formation of lithium peroxide [22, 23].

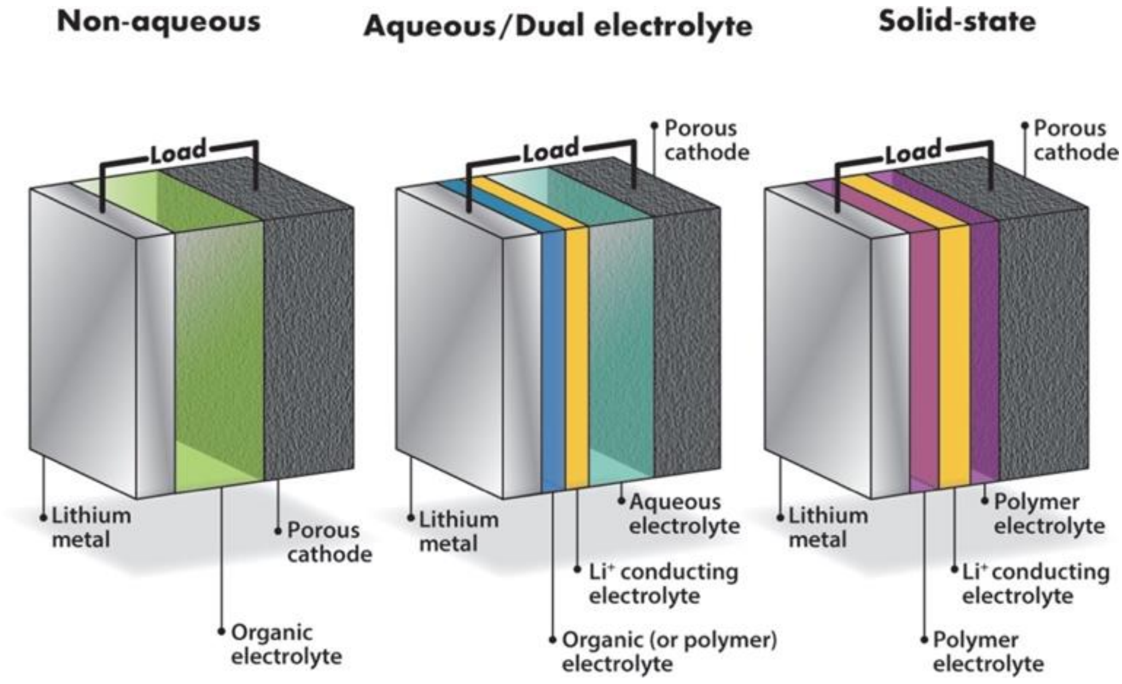


Figure 1. Schemes of aprotic (a), water / combined (b), solid-state (c) lithium-oxygen batteries. Reproduced with permission from reference [21]. Copyright 2014, WILEY-VCH.

Later in [24] it was shown that the cathodic reduction mechanism depends on the stability of the superoxide particles, which in turn correlates with the donor number of the solvent. In other words, the larger the donor number of the solvent, the more stable the superoxide particles will be formed, and the greater the discharge capacity of the lithium-oxygen battery will be.

Some known electrolytes, for example, acetonitrile, are not stable in contact with the forming reaction products, and cannot be used in lithium-oxygen batteries.

The mechanism of oxygen reduction in pyridine-based electrolytes proceeds in one stage, which leads to a decrease in the discharge capacity of a lithium-oxygen battery [24].

Currently, electrolytes based on dimethyl sulfoxide are considered optimal for lithium-oxygen batteries [24].

The effect of traces of water on the discharge capacity of a lithium-oxygen battery can occur in two ways. First, traces of water in the electrolyte can affect the morphology of the resulting reaction products. Secondly, traces of water in the electrolyte change the lifetime of the intermediate products of the oxygen reduction reaction. As was shown in [25], with increasing water content, the solubility of lithium peroxide increases, and the passivation of the electrode becomes less pronounced, which leads to an increase in the discharge capacity of the cells.

The third problem is the passivation of the porous carbon electrode by the products of the oxygen reduction reaction. It is known that lithium peroxide can crystallize on the electrode surface either in the form of a thin film and in this case the discharge capacity will not be large or in the form of mesocrystalline particles, in which case a portion of the cathode surface will remain non-passivated for a long time and the discharge capacity of the lithium-oxygen battery will be more [26]. The composition of the electrolyte plays an important role in the formation of the "optimal" precipitate. So, in electrolytes based on dimethyl sulfoxide mesocrystals are predominantly formed in the form of toroids, and in an acetonitrile-based electrolyte, a thin film of lithium peroxide is formed and it results in different discharge capacities of lithium-oxygen batteries.

The cyclic behavior of a lithium-oxygen battery can be improved by using special electrolyte compositions. The authors of [27] showed that the cyclic life of a lithium-oxygen battery increases significantly when using an electrolyte based on hexamethylphosphoramide (Fig. 2). It was found that the solubility of the products of the oxygen reduction reaction (Li_2O_2, Li_2CO_3 and LiOH) in such an electrolyte is significantly higher than in a standard electrolyte based on triethylene glycol and dimethoxyethane. In addition, the use of such an electrolyte increases the reversibility of the dissolution-precipitation reaction of lithium.

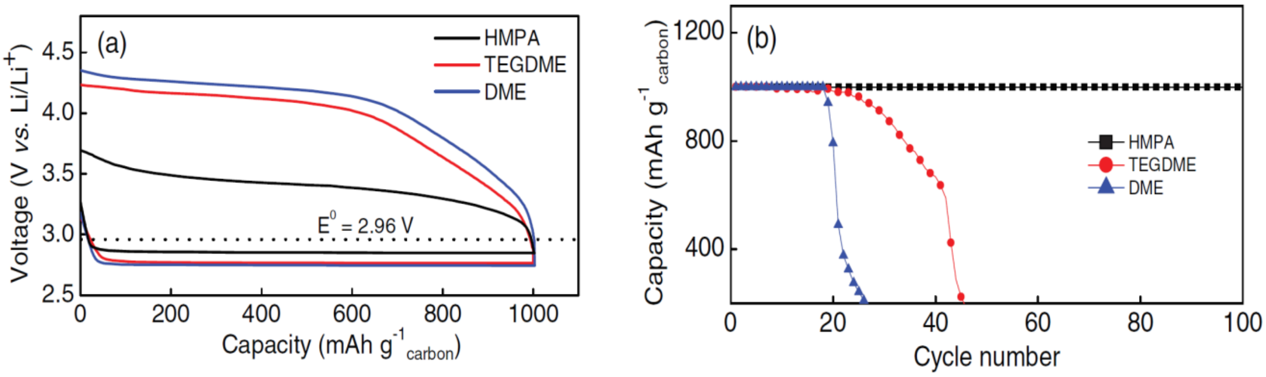


Figure 2. (a) Charge-discharge curves and (b) cycling profiles of lithium-oxygen batteries containing different electrolytes. Current density of 200 mA/g; HMPA- hexamethylphosphoramide, TEGDME – triethylene glycol-dimethoxyethane, DME – dimethoxyethane. Reproduced with permission from reference [27]. Copyright 2017, WILEY-VCH.

As catalysts for the positive electrode of a lithium-oxygen battery, various compounds of cobalt, nickel, manganese are offered. The authors of [28] proposed a method for the synthesis of a catalyst based on CoP doped with iron on carbon fabric (Fe-CoP/CC). The Li-O_2 battery based on the Fe-CoP/CC electrode demonstrated high cycling stability - more than 500 cycles without a significant voltage drop and a high discharge capacity - about 9600 mAh/g at a current density of 100 mA/g.

Perovskite-based catalysts also exhibit stable cycling and high discharge capacity when used in a lithium-oxygen battery. When using $LaMn_{0.8}Co_{0.2}O_3$ as a cathode catalyst in lithium-oxygen batteries, the specific discharge capacity of the discharge can reach 9620 mAh/g at a current of 500 mA/g, while $LaMn_{0.8}Co_{0.2}O_3$ has a longer service life compared to $LaMnO_3$ and $LaMn_{0.8}Cu_{0.2}O_3$ [29].

The most common cathode catalyst for a lithium oxygen battery is manganese oxide. When using MnO_2 synthesized on the surface of carbon multi-walled nanotubes, the discharge capacity of a lithium-oxygen battery can reach a record discharge capacity of 28517 mAh/g with a voltage of 2.82 V at a current density of 100 mA/g [30].

Unfortunately, at present, the maximum number of cycles that could be obtained for such systems is no more than 200 cycles.

2.2. Sodium-Ion Batteries

As it was mentioned before, lithium-ion batteries have some important advantages and disadvantages but here we have to underline that lithium reserves in the world are not unlimited. Chemetall reported that global lithium reserves currently amount to 28 million tons (or 150 million tons of lithium carbonate), while the annual demand for this metal is estimated at 23,000 tons (122,000 tons of lithium carbonate). If the demand for lithium is 200-300 thousand tons per year, then the case of lithium reserves on our planet will last about 90 years.

In this regard, there is a need to develop new batteries similar to lithium-ion ones. One of the potential candidates is sodium-ion batteries, which differ in that sodium is cheaper, less toxic than lithium, and its reserves are several orders of magnitude larger than lithium reserves [31, 32].

Lithium and sodium are similar in their chemical properties. However, if we compare the characteristics of lithium and sodium (Table 1), we can see that the specific capacity of sodium is much less than the specific capacity of lithium. It becomes obvious that in order for sodium-ion batteries to compete successfully with lithium-ion batteries, sodium-ion batteries must be much cheaper, and their specific energy should be comparable to the specific energy of lithium-ion batteries.

Table 1. Comparison of lithium and sodium characteristics

	Lithium	Sodium
Cation radius, nm	0.07	0.1
Molar mass, g/mol	6.9	22.98
Standard electrode potential, V (Li/Li^+)	0.0	0.3
Theoretical specific capacity, mAh/g	3829	1165
The cost of lithium carbonate (sodium), USD/t	5000	150

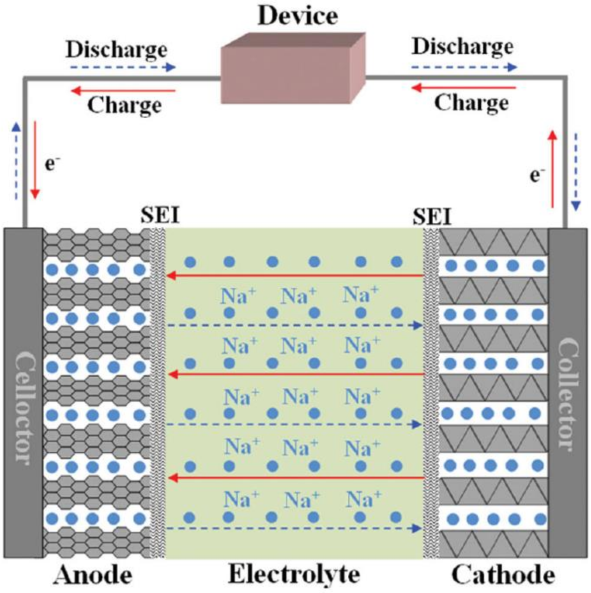


Figure 3. The principle of operation of a sodium-ion battery. Reproduced with permission from reference [33]. Copyright 2015, WILEY-VCH.

The principle of operation of lithium-ion and sodium-ion batteries is the same. When charged, alkali metal ions are extracted from the material of the positive electrode and embedded in the material of the negative electrode. When discharged, the ion motion reverses (Figure 3). This means that the design of the sodium-ion battery will be similar to the design of the lithium-ion battery, and the cost will be determined by the cost of the functional materials in the sodium-ion battery.

Currently, a large number of various functional materials for sodium ion batteries were synthesized. There are anode materials, the theoretical capacity of which is close to 2500 mAh/g. The discharge potentials of sodium-containing materials are slightly lower than the potentials of lithium-containing materials, but in general, the picture is similar for these two types of materials. As the anode material, the greatest hopes are placed on lithium titanate, hard carbon, germanium and phosphorus.

An anode material based on sodium titanate ($Na_2Ti_3O_7$) is capable of incorporating up to two sodium ions per molecule, while the discharge potential is about 300 mV (vs. Na / Na^+), which distinguishes this material from lithium titanate, whose working potential is noticeably more positive.

$$Na_2Ti_3O_7 + 2Na^+ + 2e \leftrightarrow Na_4Ti_3O_7 \tag{3}$$

Q_{theor} = 177 mAh/g (Theoretical specific capacity of sodium titanate)

The ability to operate at high currents is explained by the small particle size of sodium titanate and the increase in electronic conductivity due to the carbon coating (Fig. 4).

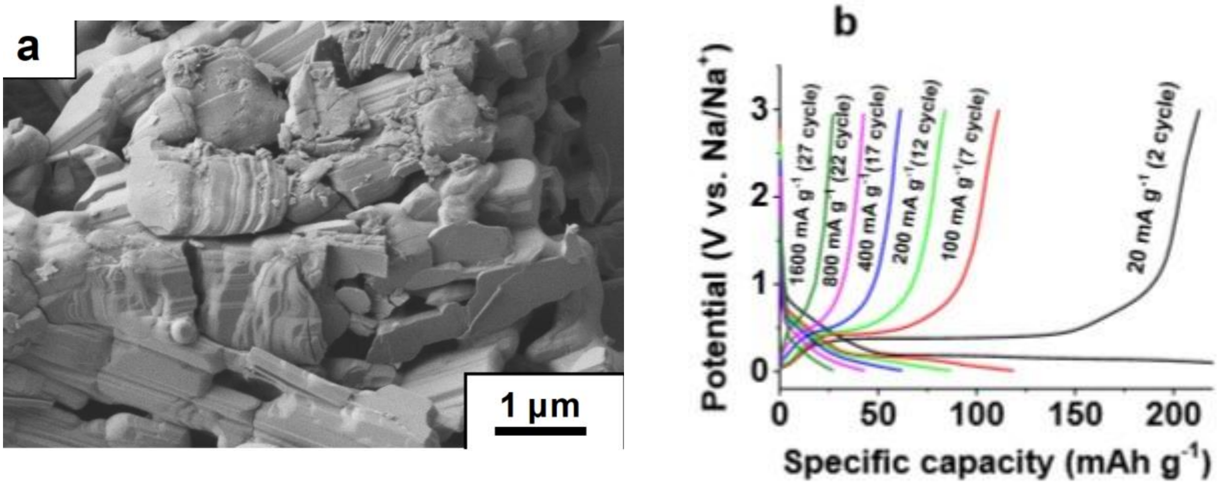
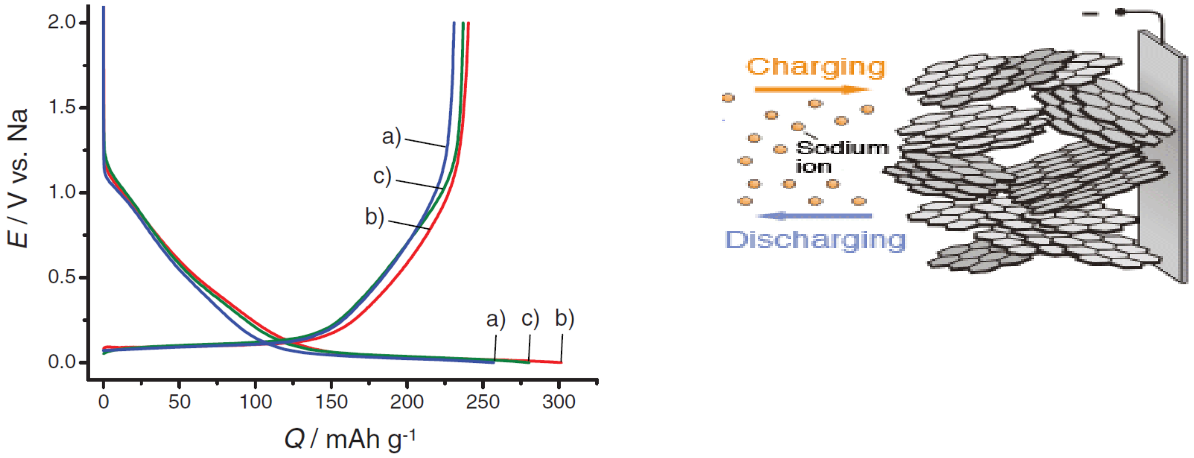


Figure 4. SEM image (a) and charge-discharge curves at various current densities (b) of sodium titanate. Reproduced with permission from reference [34]. Copyright 2018, Springer Nature.

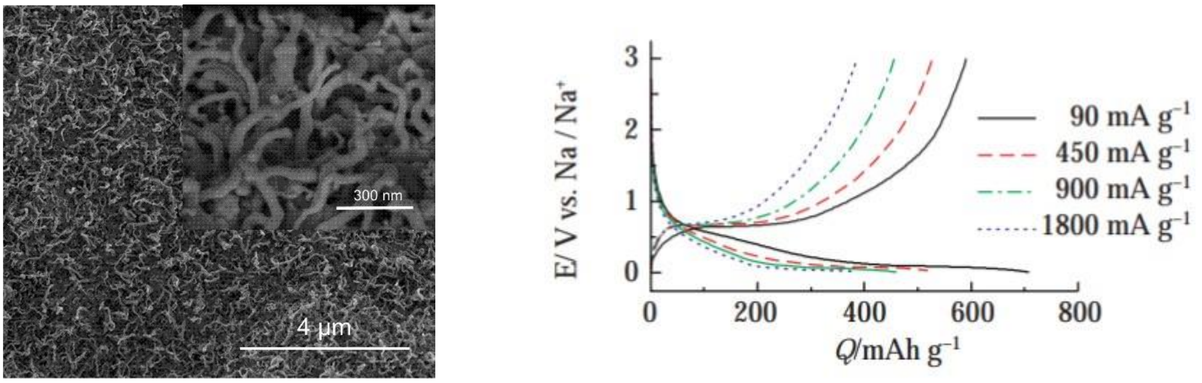
Another candidate for the role of the anode material for the sodium ion battery is a hard carbon. According to research of various scientific groups, the specific capacity of carbon during the intercalation of sodium can reach 350 mAh/g. In this case, the potential of reversible intercalation is close to the potential of the sodium electrode (Fig. 5).



a) **b)**

Figure 5. Charging-discharge curves of hard carbon (a) and a schematic representation of the process of insertion-extraction of sodium ions in hard carbon (b). Reproduced with permission from reference [35]. Copyright 2011, WILEY-VCH.

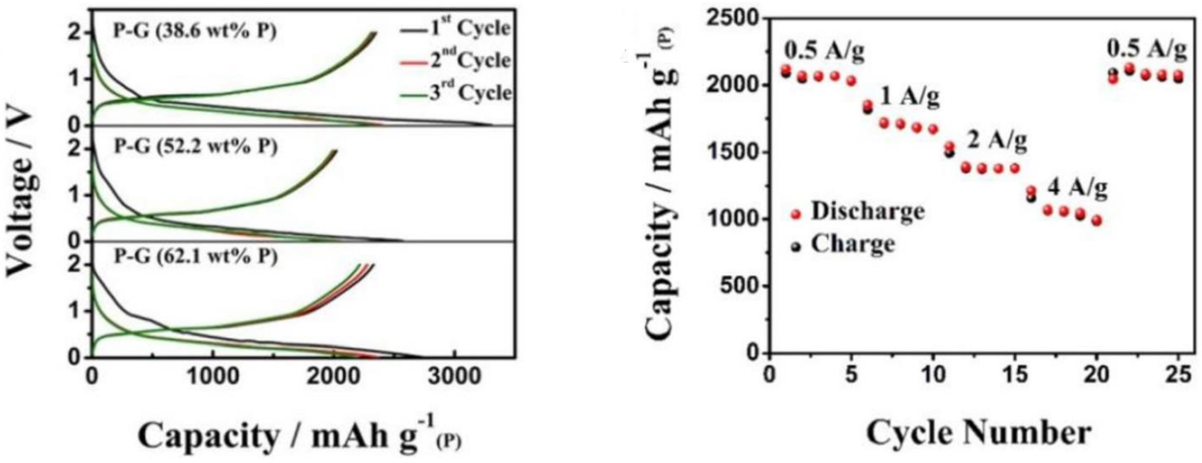
The new anode material for the sodium-ion battery is germanium. Nanostructured germanium synthesized by electrochemical deposition from germanium-containing aqueous solutions shows high values of discharge capacity, stable cycling, and the ability to operate at high current densities (Fig. 6).



a) b)

Figure 6. SEM image (a) and charge-discharge curves (b) of germanium filaments upon insertion-extraction of sodium. Reproduced with permission from reference [36]. Copyright 2018, Elsevier.

The most promising candidates for the role of the anode material of the sodium-ion battery are composites based on red phosphorus. The specific capacity of the phosphorus-carbon composite reached 2500 mAh/g, which explains the great interest in this material. But it has a large degradation during cycling. Composites of phosphorus with graphene are able to eliminate this disadvantage; in addition, such composites must be able to work at high current densities, which is important for the battery (Fig. 7).



a) b)

Figure 7. Charge-discharge curves (a) and the dependence of capacity on current density (b) during cycling of electrodes based on red phosphorus. Reproduced with permission from reference [37]. Copyright 2015, WILEY-VCH.

One of the new anode materials for the sodium-ion battery is phosphorus sulfide. The process of insertion of sodium into phosphorus sulfide can be described by the following reaction:

$$P_4S_3 + 18\,Na^+ + 18\,e^- \leftrightarrow 3\,Na_2S + 4\,Na_3P \qquad (4)$$

The occurrence of this reaction is confirmed by X-ray diffraction patterns recorded on phosphorus sulfide electrodes before and after cycling (Fig. 8a). The charge – discharge curves are quite stable even at a current density of 100 mAh/g (Fig. 8b).

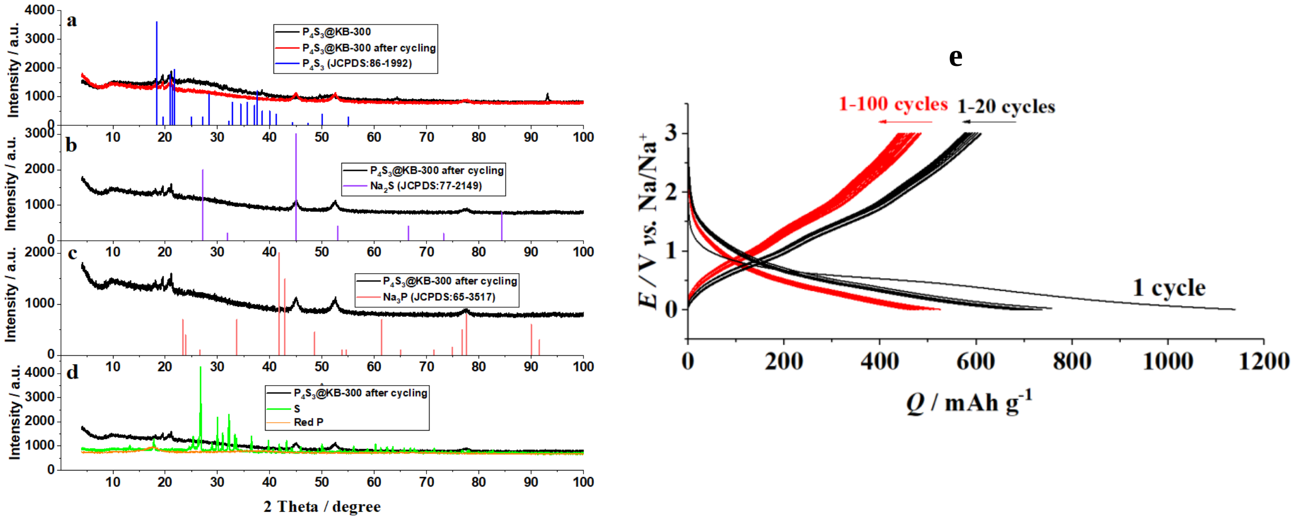


Figure 8. X-ray diffraction spectra: (a) PS-KB-300 composite before and after cycling, (b) comparison of the spectrum of the PS-KB-300 composite after cycling with the Na_2S standard, (c) comparison of the spectrum of the PS-KB-300 composite after cycling with the Na_3P standard, (d) comparison of the spectrum of the PS-KB-300 composite after cycling with the spectra of sulfur and phosphorus, (e) charge-discharge curves at various current densities. Reproduced with permission from reference [38]. Copyright 2019, Elsevier.

Among the various cathode materials, layered oxides are the most popular group. By analogy with lithium cobaltate, sodium cobaltate $NaCoO_2$ was originally synthesized. Unfortunately, a common drawback of layered oxides is the strong degradation during the complete extraction of sodium due to structural changes. More or less stable cycling can be achieved with incomplete extraction of sodium from $NaCoO_2$, however, this leads to a low specific discharge capacity. More stable cathode composition are layered oxides based on the stoichiometry of sodium and transition metals. For example, cathode based on $Na_{0.55}[Ni_{0.1}Fe_{0.1}Mn_{0.8}]O_2$ is characterized by stable cycling with discharge capacity of 221.5 mAh/g [39].

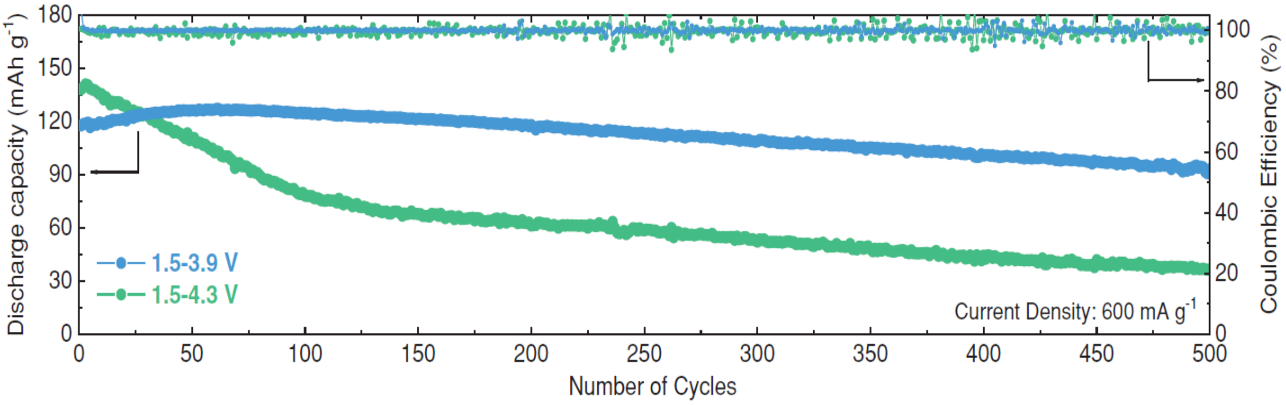


Figure 9. Capacity fading of P2-$Na_{0.55}[Ni_{0.1}Fe_{0.1}Mn_{0.8}]O_2$ in different voltage windows at a current density of 600 mA/g. Reproduced with permission from reference [39]. Copyright 2019, WILEY-VCH.

The researchers placed great hopes on sodium iron phosphate $NaFePO_4$. However, sodium iron phosphate with the olivine structure turned out to be electrochemically inactive, and $NaFePO_4$ with the maricite structure was characterized by a low specific capacity. It was possible to increase the specific capacity only due to the mechanochemical activation of sodium iron phosphate with the maricite structure [40, 41].

The cathode materials based on sodium vanadium phosphate $Na_3V_2(PO_4)_3$ with the NASICON structure were proposed for sodium-ion batteries back in 2010. Many researchers propose using this material not only as a positive, but also as a negative electrode. The charge – discharge curves have clear areas, which indicates a two-phase mechanism of the sodium introduction – extraction process (Fig. 10). The material shows a specific capacity close to theoretical and a weak dependence of the discharge capacity on current density [42, 43].

Na_2FePO_4F demonstrates outstanding rate capability and a structural stability, showing 83% capacity storage after 100 cycles at high current density (2C). Taking into account the remarkable electrochemical properties, as well as its low cost, safety and simple synthesis, Na_2FePO_4F is a promising cathode material for sodium-ion batteries.

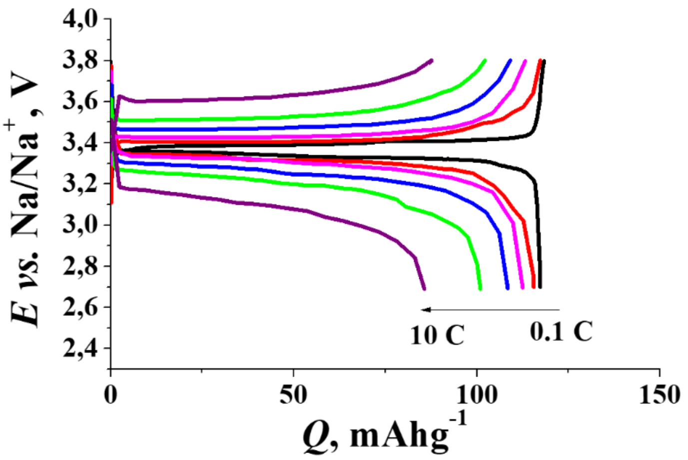
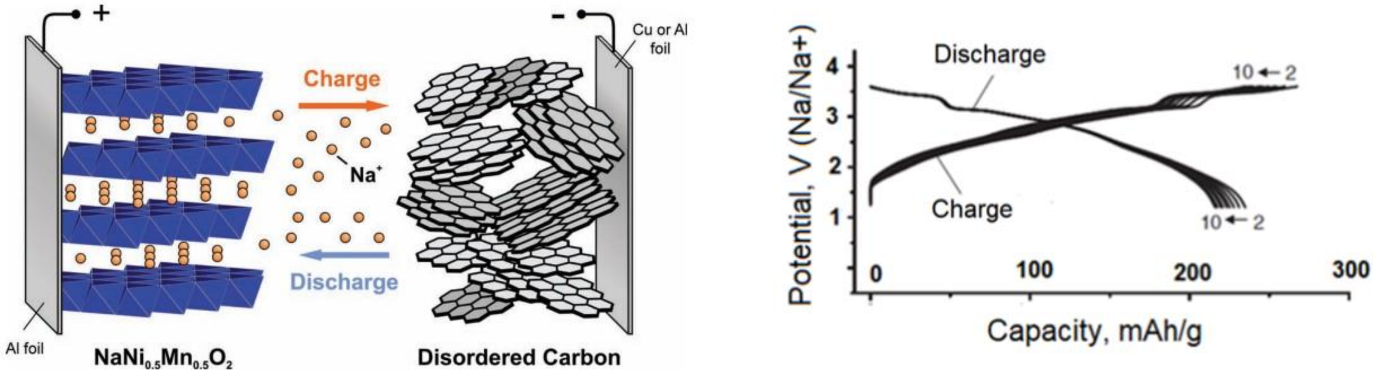


Figure 10. Charge-discharge curves of an electrode based on $Na_3V_2(PO_4)_3$ at various current densities. Reproduced with permission from reference [43]. Copyright 2017, Springer Nature.

Various prototypes of sodium ion batteries are currently described and tested. One example is a battery containing a negative electrode based on carbon and a positive electrode based on $NaNi_{0.5}Mn_{0.5}O_2$. It has an average voltage of about 3 V, and the specific capacity of the prototype battery, calculated on the mass of active substances, was 220 Wh/kg [44]. At the same time, the battery showed insufficient cycling stability. The loss of capacity over 10 cycles was about 10% (Fig. 11).



a) b)

Figure 11. Schematic representation (a) and charge-discharge curves (b) of a coin-type hard carbon/ $NaNi_{0.5}Mn_{0.5}O_2$ battery. Reproduced with permission from reference [35]. Copyright 2011, WILEY-VCH.

Another example of a battery prototype consisted of cathode based on $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ and antimony anode (Fig. 12). The specific energy of such a prototype was about 320 Wh/kg (calculated for mases of functional electrode materials). An increase in the battery capacity was achieved by increasing the specific capacity of the negative electrode manufactured from macroporous Sb/MgF_2) [45].

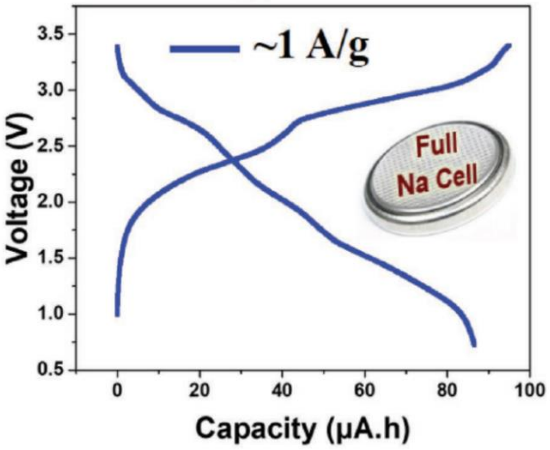


Figure 12. Charge-discharge curves of the prototype sodium-ion battery based on $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ and Sb/MgF_2. Reproduced with permission from reference [45]. Copyright 2018, WILEY-VCH.

A prototype of sodium-ion battery based on sodium vanadium phosphate and sodium titanate was developed by authors [46]. The specific energy of such a prototype was about 220 Wh/kg (based on the masses of active substances). The practical energy density of the battery is expected to be around 120 Wh/kg. In addition, it was shown that such a battery can operate at negative temperatures (up to −30 °C) (Fig. 13).

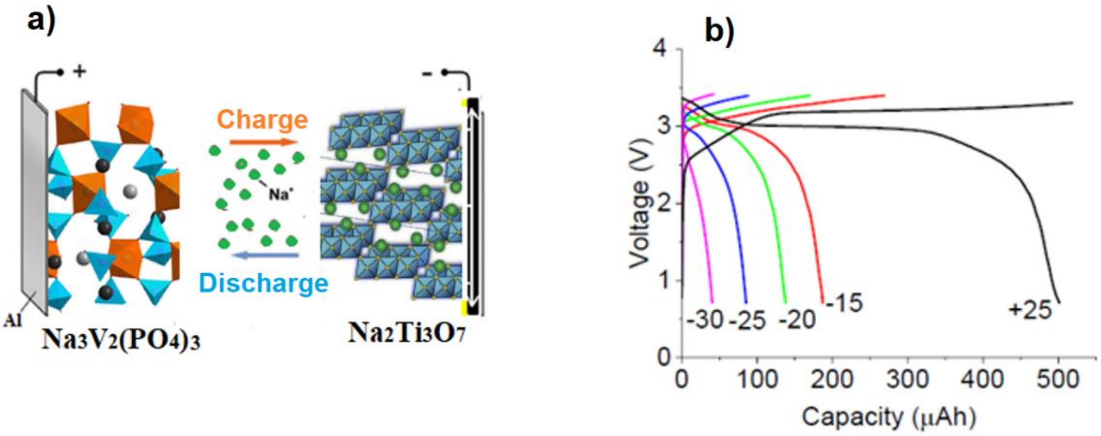
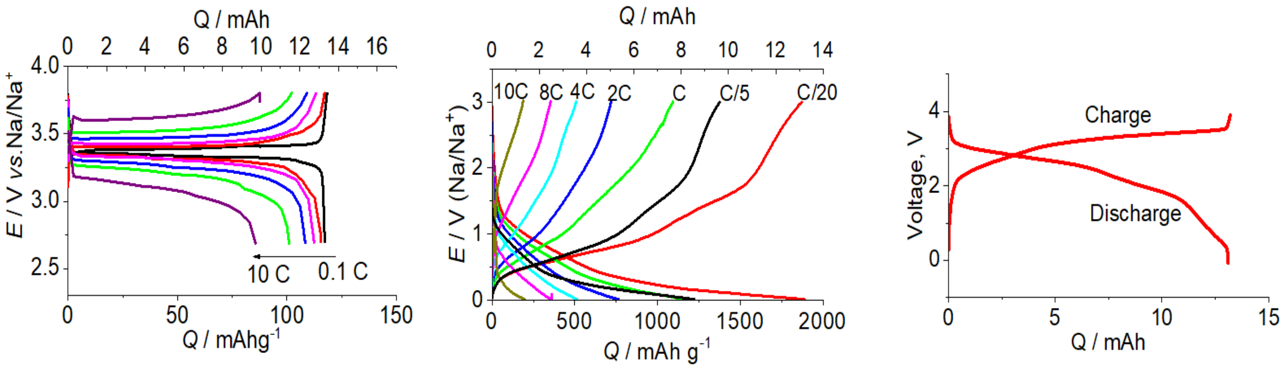


Figure 13. Schematic representation (a) and charge-discharge curves (b) of the prototype sodium-ion battery based on sodium vanadium phosphate and sodium titanate. Reproduced from open access reference [46].

A promising electrochemical system of a sodium-ion battery based on sodium vanadium phosphate and a phosphorus composite with carbon was developed (Fig. 14). The specific energy of the battery calculated on the mass of active substances, is about 340 Wh/kg.

Sodium-ion batteries cannot completely replace lithium-ion batteries, but can be used as efficient stationary energy storage devices. In terms of specific energy, sodium-ion batteries today are somewhat worse than lithium-ion batteries, however, in terms of cost of production and the cost of electricity, sodium-ion batteries will undoubtedly win.



a b c

Figure 14. (a) Charge-discharge curves of sodium vanadium phosphate at various current densities; reproduced with permission from reference [43], copyright 2017, Springer Nature. (b) Charge-discharge curves of phosphorus-carbon composite at various current densities; reproduced from open access reference [47]. (c) Charge-discharge curves of the battery based on sodium vanadium phosphate and a phosphorus-carbon composite at current density of 0.1C; the Figure 14c made by the authors of this article.

2.3. Lithium-Sulfur Batteries

Lithium-sulfur batteries are characterized by the highest theoretical specific energy (2600 Wh/kg) among various batteries [48]. This value is almost 5 times higher than the theoretical specific energy of modern commercial lithium-ion batteries. Furthermore, sulfur is the most abundant element in the earth's crust, has a low cost, and is relatively safe for humans and the environment [49]. Over the past few decades, research has been intensively carried out around the world to create lithium-sulfur batteries [48, 50], however, lithium-sulfur batteries that meet all the requirements of the market have not yet been created.

The main problems are low specific energy of lithium-sulfur batteries, which today does not exceed 420 Wh / kg [48], severe degradation during cycling [48], high self-discharge.

The main problems that arise in the development of commercial lithium-sulfur batteries are related to the fact that sulfur positive electrode in the battery is liquid cathode [51]. For the efficient operation of lithium-sulfur batteries, a great deal of electrolyte is required, which leads to a decrease in the specific energy of lithium-sulfur batteries [51]. The reasons for self-discharge of lithium-sulfur batteries are the chemical interaction of lithium metal electrode with a sulfur and with lithium polysulfides in the electrolyte [53] and corrosion of the current collector [54]. The operation diagram of the lithium-sulfur battery is shown in Figure 15.

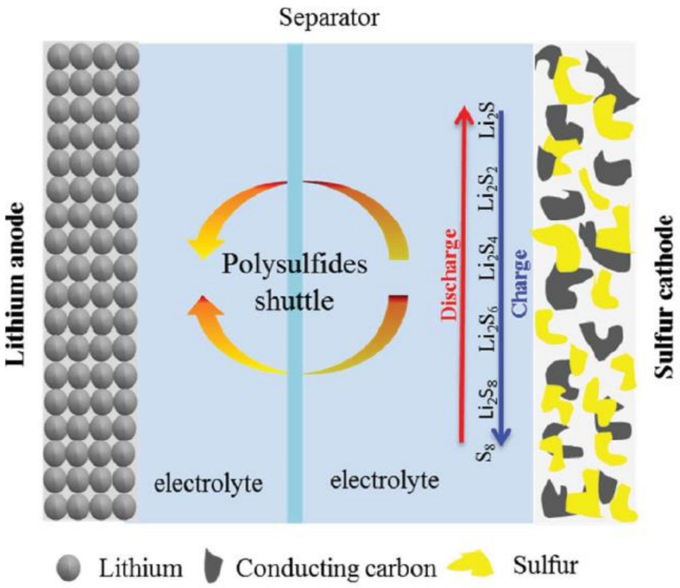


Figure 15. Schematic representation of the processes in a lithium-sulfur battery. Reproduced with permission from reference [52]. Copyright 2017, WILEY-VCH.

To solve these problems, several ways are proposed. One way is the deposition of carbon materials of different nature [55] as additional layer on the surface of the separator, which will impede the diffusion of lithium polysulfides to the anode. Other ways are the use of second membrane between the sulfur electrode and the separator that prevents the movement of lithium polysulfides to the lithium electrode [56-58], selection of the optimal electrolyte containing various additives [59-61], improving the composition of the sulfur electrode in order for reduce the dissolution of lithium polysulfides in the electrolyte [62, 63]. In other words, all techniques for reducing self-discharge of lithium-sulfur cells are aimed at preventing the pass of sulfur and lithium polysulfides to the lithium negative electrode.

Authors [64] have presented the results of developing of novel cathode substrate that enables a Li–S battery to deliver an initial capacity of as high as 1415 mAh /g at 0.1 C. Such cathode substrate was made from boron carbide decorated activated cotton fiber. The Li-S battery stably operated for 3000 cycles with a high coulombic efficiency of 99.24 %. LiF can used as additive to the electrolyte. LiF forms an artificial membrane that hinders the transport of polysulfides [65]. The using of 3D network-like nanocomposite effectively adsorb lithium polysulfides [66]. Such composite was obtained via the well-distributed composition of the carbon nanotubes with nitrogen-doped carbon nanosheets as well as Co nanoparticles from carbonization of the nitrogen-rich bio-MOF-100 nanosheets at an inert atmosphere. Specific capacity of Li-S battery with such of 3D network-like nanocomposite reached 972.4 mAh/g at 2C under current density of 2.0 mg/cm^2 with the capacity decay of 0.05 % per cycle during the 1000 long-term cycles.

2.4. Comparison of the characteristics of post-lithium-ion batteries

The specific energy of any battery depends on several factors, namely, the specific capacity of cathode and anode materials, the type of electrolyte used, the voltage of the electrochemical system, and the design of the battery. The type of battery assembling (roll, stack) as well as the material used for the battery case (metal or plastic) have a significant impact on the specific energy of the battery as a whole. That is why, for comparison of different types of batteries, it is convenient to compare the theoretical specific energy of the battery, i.e. the energy of the battery, divided only on the masses of active substances. The table 2 shows the characteristics of various post-lithium-ion batteries. As can be seen from the table, lithium-oxygen batteries have the best values of theoretical specific capacity. At the same time, researchers estimate the best characteristics for commercial batteries will be inherent in lithium-sulfur batteries.

Table 2. Characteristics of post-lithium-ion batteries

	Lithium-oxygen battery	Sodium-ion battery	Lithium-sulfur battery
Positive (cathode) electrode material	O_2 in porous matrix (activated carbons, carbon nano-tube, graphene, TiC, Co_xO_y and Ni). Catalyst: Au, Au–Pt, Ru and RuO_2 [69]	$NaCoO_2$, $Na_2V_3(PO_4)_3$, $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$, Na_2VPO_4F, $NaFePO_4$, $Na_3V_2(PO_4)_2F_3$, $NaFeP_2O_7$, $Na_2CoP_2O_7$, $Na_2MnP_2O_7$, $Na_3V_2(PO_4)_2O_2F$ $Na_4Fe_3(PO_4)_2P_2O_7$, [67- 69]	Cepa, polyaniline@S composite, polythiophene@S composite, TiO_2@S composite [71]
Negative (anode) electrode material	Lithium metal	Hard carbon, Ge, P, Sn, Sb, P@C composites, $Na_3Ti_2O_7$, $NaTi_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, Sb_2Se_3 [66, 67, 69]	Lithium metal; lithiated graphite
Electrolyte	Salts: $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$. Solvents: AN, DMSO, DMFA, PC, EC, DME, DEC, ionic liquids [22-30]	Salts: $NaPF_6$, $NaClO_4$. Solvents: PC, EC, DME, DEC [34-43, 67, 68, 70]	Salts: $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, $LiBF_4$. Solvents: DME, TGF, DO [59-66, 71]
Average discharge voltage, V	2.7 – 2.8	2 – 3.3	2.05 – 2.1
Theoretical specific energy, Wh/kg	7200 [71]	350 – 500 [69]	2600 [71]
Estimated specific capacity of commercial battery, Wh/kg	500 [71]	150 – 320 [71]	600 [71]

* acetonitrile (AN), dimethyl sulfoxide (DMSO), dimethylformamide (DMFA), propylene carbonate (PC), ethylene carbonate (EC), dimethoxyethane (DME), diethyl carbonate (DEC), TGF, dioxolane (DO)

4. CONCLUSIONS

The analysis of the last publications on lithium-ion and post-lithium-ion batteries was done. Among post-lithium-ion batteries lithium oxygen, sodium-ion and lithium-sulfur batteries appear as most perspective and are intensively developed now. Some perspective directions of R&D are shown. In spite of a large demand for post-lithium-ion batteries they are not commercialized still as an additional R&D has to be done though the commercialization is approaching. Undoubtedly, post-lithium-ion batteries will be the successors of modern lithium-ion technologies. Future concepts of post-lithium-ion batteries focus on new approaches to solve the problem of achieving specific energy close to 500 Wh/kg. However, most of them, such as lithium-oxygen batteries, are still far from commercial use. In the near future, sodium-ion and lithium-sulfur batteries and batteries based on them represent the most real possibility of commercial use.

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