Review of Materials for Electrodes and Electrolytes of Lithium Batteries

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Article history	Abstract
	Lithium-ion batteries are still efficient and reliable energy storage systems and are widely used in portable electronics and electric vehicles. This review describes the types of currently existing lithium batteries, systems with anodes, cathodes and electrolytes made of various materials, and methods for their study. Specifically, it begins with a brief introduction to the principles of lithium-ion batteries operation and cell structure, followed by an overview of battery research methods. Particular attention is paid to the use of nanosized particles for the modification of electrodes and electrolytes, as well as the copolymerization of individual polymers of the gel-polymer electrolyte. The review analyzes possible future developments and prospects for post-lithium batteries.

1. INTRODUCTION

Ever-increasing negative impacts on the environment promote the active development of eco-friendly technologies not only for energy generation, but also for energy storage. Since wind and solar power plants, which are to become the basis for generating green electricity, cannot operate at full capacity around the clock and year-round, devices to store energy must be created [1]. Due to low self-discharge and a large number of charge/discharge cycles, lithium-ion batteries (LIBs) are most preferred for use in alternative energy. LIBs, as one of the efficient energy storage devices, are used in many fields including portable equipment and electric vehicles, power plants [2]. Until now, Li-primary batteries (single action cell) are still widely employed in cardiac pacemakers [3]. However, the primary batteries are not rechargeable, resulting in high cost, serious waste, and environmental pollution.

The first lithium current sources with an aprotic electrolyte appeared in the early 1970s [4]. The development of primary lithium batteries with a lithium anode proved to be successful, but the creation of secondary lithium batteries (repeated cell on which the electrode reactions are reversible) has many difficulties.

The review systematizes literature data on developments in the field of lithium batteries, describes the characteristics of materials for electrodes and electrolyte and methods for their measurement, discusses the main problems and possible solutions. Particular attention is paid to the use of nanoscale materials and their impact on the mechanical and electrical characteristics of batteries. Advanced materials that can potentially replace lithium in batteries are also described.

2. CLASSIFICATION OF RECHARGEABLE BATTERIES WITH LITHIUM

According to the principle of operation, lithium batteries can be divided into three groups: lithium batteries with lithium metal (LMBs), LIBs and lithium polymer batteries (Li-Pol) [5]. As a rule, a lithium battery consists of four parts: positive and negative electrodes (anode and cathode), separator and electrolyte (Fig. 1). Electrodes are an active materials deposited on a metal current collector, for example copper or aluminum, with an electrically conductive additive and a binder. The anode is the electrode where the oxidation reaction occurs, while the cathode is the electrode where the reduction reaction occurs.

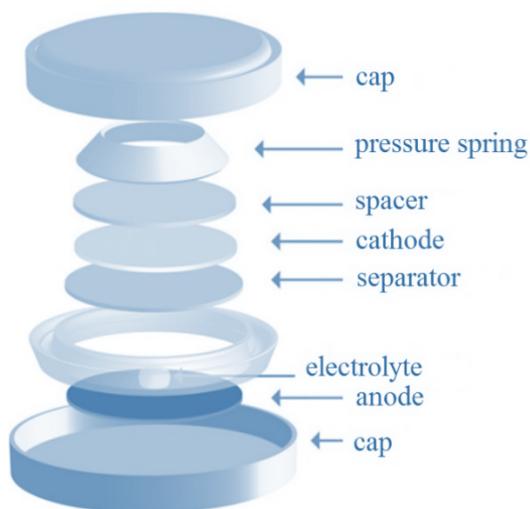* Corresponding author: E. Podlesnov, e-mail: epodlesnov@itmo.ru

Fig. 1. Constituent elements of a lithium cell type CR-2032.

2.1. Lithium batteries

Lithium is one of the best anode active substances on Earth. It has a high theoretical specific capacity (3860 mA·h/g), a low redox potential (3.040 V relative to a standard hydrogen electrode) and a low density (0.534 g/cm^3). Lithium, the lightest member of the alkali metal group, has the smallest atomic radius of all metals. These features provide Li metal with ultrahigh capacity and quick transfer nature [6]. Despite so many advantages, the practical application of the lithium anode is limited because of lithium dendrites formation during cycling [7]. Dendrites can pierce the separator, which leads to a short circuit and battery failure. Also, lithium batteries do not tolerate freezing or overheating.

Since the 1960s, the proposed methods to suppress dendrite growth can be classified into four categories [3]:

1. LiX alloy (X = Al, B, Si, Sn, C, etc.). Substituting Li metal with LiX alloy can significantly reduce the dendrite problems, because Li is in its ionic rather than metallic state. Unfortunately, the alloy electrodes can only survive limited cycles due to large volume changes during cycling [6]. However, the carbon electrode partly guarantees safe operation, yet large capacity is drastically sacrificed from 3860 to 372 mA·h/g.

2. Organic electrolyte and Li metal/electrolyte interface modifications. In the 1950s, Li metal was found to be successfully stabilized in some non-aqueous solvents due to the formation of a passivation film on the Li surface [8]. Intensive research activities have been devoted to seeking the proper Li salts, solvent, electrolyte additives, and artificial passivation film. However, the function of the passivating film gradually becomes incapable in rechargeable LMBs due to dendrite growth during repeated Li depositing/stripping.

3. Solid-state electrolytes. The inorganic, polymer, and their hybrid solid-state electrolytes are expected to have a high shear modulus and thoroughly abandon the use of flammable non-aqueous liquid electrolytes, thus drastically enhancing the safety performance of LMBs. In contrast, the present ionic conductivity of these systems is typically between 10^{-8} and 10^{-5} S/cm at room temperature [9,10] and far below that of the non-aqueous liquid electrolyte (10^{-3} S/cm) [11–13].

4. Structured anode design. The revolution in nanomaterial and nanotechnology undoubtedly innovates Li dendrite inhibition research by constructing a novel matrix for Li depositing and designing separator/anode integration to modify Li ion depositing behavior [3].

2.2. Lithium-ion batteries

A revolution in electrical engineering was made by the creation of LIB. The pioneer in this area was the SONY company [14], which already in the early 90s of the XX century began to use Li-ion technologies in its portable electronics. There is no metallic lithium in the Li-ion system, and the electric current in the external circuit is provided by the transfer of lithium ions from the anode to the cathode [15]. The creators of LIB, John B. Goodenough, M. Stanley Whittingham and Akira Yoshino, were awarded with the Nobel Prize in Chemistry 2019 "for the development of lithium-ion batteries". Stanley Whittingham showed the possibility of reversible insertion-extraction of lithium in layered sulfide transition metal materials. Unlike acid batteries, substances in LIBs do not dissolve, they change the concentration of lithium ions and, accordingly, the number of electrons in the conduction band, as well as the degree of oxidation of the transition metal. Goodenough showed that $LiCoO_2$ could be used as an electrode material.

The potential of carbon electrodes with a small amount of intercalated lithium can be higher than the potential of a lithium electrode by 0.5–0.8 V. Yoshino suggested using an electrode based on carbon materials, which made it possible to ensure stable operation of LIB, maintain its initial capacity, applied voltage and current for as long as in the nickel-cadmium and nickel-metal hydride batteries widely used at that time. The morphological stability of the electrodes is ensured by a small change in the specific volume of the carbon matrix (no more than 10%) during the introduction/extraction of lithium ions. However, frequent cycling leads to a significant loss of battery capacity — depletion is one of Li-ion's most severe drawbacks. The number of charge and discharge cycles is limited to 500–

1000 cycles, then the capacity reduces and degradation increases [16]. The main advantages of LIBs are high energy density, which allows electronic equipment to work longer without recharging, and low self-discharge rate (loss of charge without use). They lose much less energy than other rechargeable cells. Current LIBs are not an ideal solution, but new lithium-ion technologies are constantly developing and improving.

2.3. Lithium polymer batteries

Lithium polymer battery (Li-Pol) is an advanced design of LIB that uses a polymer material as the electrolyte. Recently, this type of battery has been widely used in mobile phones and portable equipment [17]. The advantages of Li-Pol are variability in shape, the possibility of execution in a flexible case, and safety due to gel or solid electrolyte. The main disadvantages are the high cost of production and thin case wearing capacity.

3. BATTERY TEST METHODS

The main battery characteristics are its operating voltage, capacity, working life and power. This section describes methods for testing the electrical and performance characteristics of a battery.

Cyclic voltammetry (CV) is one of the simplest methods for studying the electrochemical properties of electrodes. CV allows to obtain information about the ongoing redox reaction in the battery cell [18], to determine the voltages, at which reduction and oxidation reactions occur, and to evaluate quantitative information at an unknown concentration of substances [19]. The essence of the method is to measure the current with a linear change in the applied voltage in the process of charging and discharging the cell. The measurement result is a voltammogram (Fig. 2), which is the dependence of the measured current on the voltages applied to the electrodes.

Cycling is a traditional battery cell performance test that evaluates the capacity of a cell at various discharge and charge rates over a given number of cycles. The essence of the method is to repeatedly discharge and charge the battery cell and measure the capacity at each cycle. The result of cycling (Fig. 3) is a graph of the dependence of the capacity of the battery cell on the serial number of the cycle. A single discharge or charge of a battery cell is considered a cycle. C-rate is a measure of the charge/discharge rate of a battery cell relative to its capacity.

Theoretical capacity is defined as the number of ions that can be stored per unit mass of the electrode material [21]:
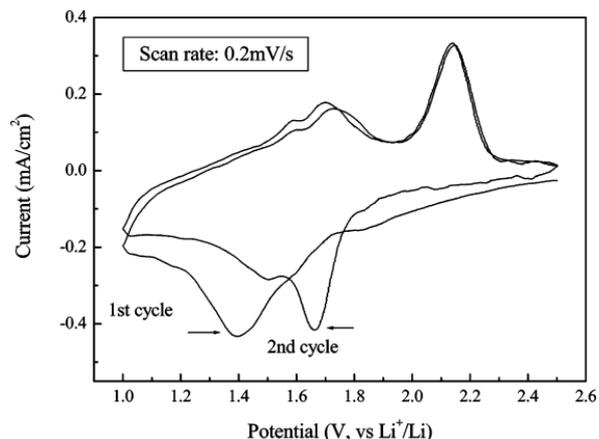
$$C_t = 26800 \frac{n}{M},$$ (1)

Fig. 2. Cyclic voltammograms of electrode based on anatase nanorods. Reprinted with permission from Ref. [20], © 2004 American Chemical Society.
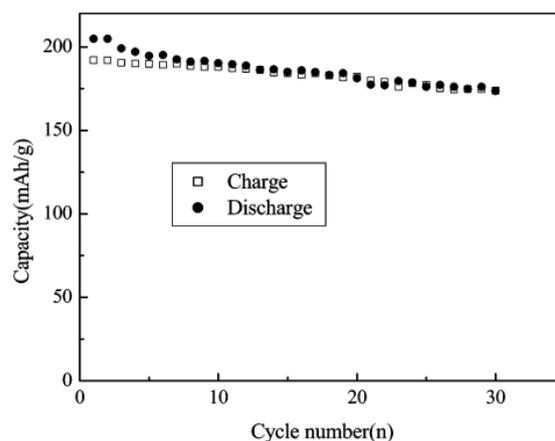

Fig. 3. Cycle life of the electrode made by the anatase nanorods at discharge-charge current density of 50 mA·h/g at 20 °C. Reprinted with permission from Ref. [20], © 2004 American Chemical Society.

where C_t (mA·h/g) is a theoretical capacity, n is a number of electrons involved in the electrochemical reaction, M (g/mol) is a molar mass of the active material.

For example, consider $LiCoO_2$ (the upper delithiation voltage of $LiCoO_2$ cannot exceed 4.2 V relative to Li/Li$^+$, which means that only half of the theoretical capacity of $LiCoO_2$ can be achieved) and graphite; the electrochemical reaction is as follows:

$$LiCoO_2 \leftrightarrow \frac{1}{2} Li^+ + \frac{1}{2} e^- + Li_{0.5}CoO_2,$$

$$Li^+ + C_6 + e^- \leftrightarrow LiC_6.$$ (2)
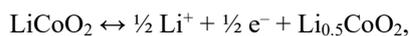
Then the theoretical capacities of $LiCoO_2$ and graphite are 137 and 372 mA·h/g, respectively [22].

The specific energy W (W·h/kg) that an electrochemical cell can provide is determined from the operating voltage V of the cell and its electrochemical specific capacity C_t:
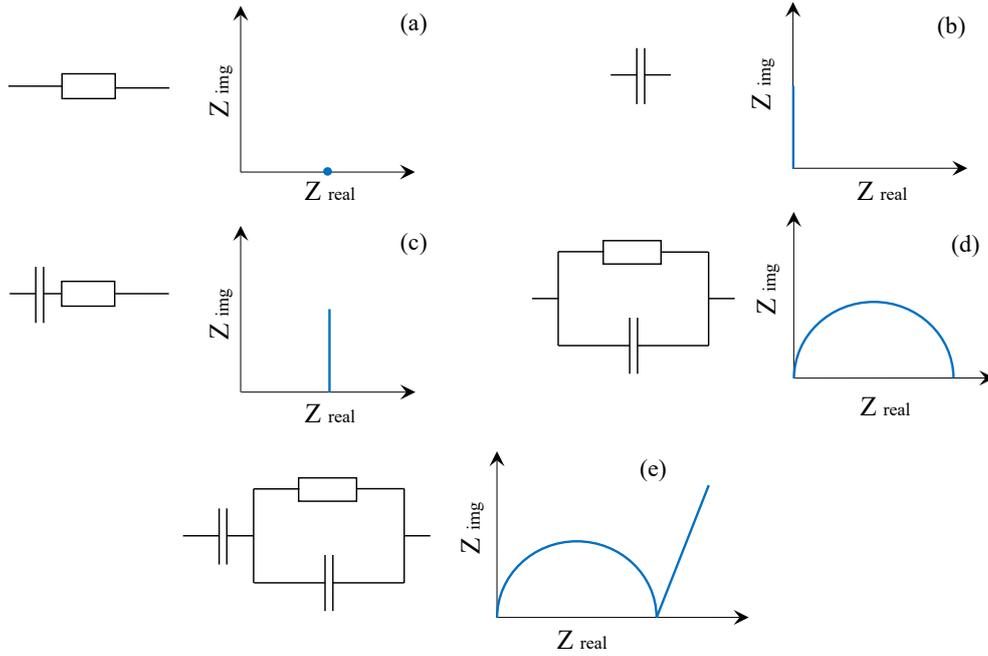
$$W = V \cdot C_t.$$ (3)

Fig. 4. The plots and their equivalent circuits for (a) a pure resistor, (b) a pure capacitor, (c) a capacitor and a resistor in series, (d) a capacitor and a resistor in the parallel combination, and (e) a leaky system. Adapted from Ref. [27].

Battery working life is also an important performance characteristic. In fact, this is the number of charge/discharge cycles that a battery can perform, while losing no more than 20% of its initial capacity. Together with the working life, the Coulomb efficiency is considered — the ratio of the discharge and charging capacities, in the ideal case, equals 100%.

The basis of the battery functioning mechanism is the transfer of ions and electrons. Since the measure of the speed of the charges is conductivity, the understanding of the conductivity processes in LIBs is a key problem of phenomena determining the operation of the battery and asking ways to improve characteristics. Since there is ion and electronic conductivity, the improvement of the capacity of modern LIBs can be achieved by an increase in electronic conductivity and diffusion ability of ions in anode and cathode materials [23].

The electrons are supplied by the current collectors for electrodes, while lithium ions move through the active material and pores, thereby creating a pathway through the electrolyte. It should be noted that electron transfer through the electrolyte is undesirable because it could cause severe damage to the cell and may result in the explosion of the cell, leading to serious hazards. The electronic conduction in electrodes should occur fast; therefore, a conducting additive is generally used alongside the active materials [24].

Electrochemical impedance spectroscopy (EIS) is a method for studying the processes associated with the transition of electrons from an electrode to a current collector, the conductivity of electrons in an electrode, the

movement and diffusion of ions, and the formation of a double electric layer on the surfaces of electrodes [25]. The EIS method does not destroy the battery cell in the process, which allows it to be examined at various stages of operation [26]. To varying extent, battery components are sources of impedance of a resistive, capacitive, or inductive nature. The essence of the method is to apply an alternating current signal to the battery cell in the frequency range and measure the system response. The result of the EIS is the amplitude-phase frequency response, which is a graph of the dependence of the imaginary part of the impedance on its real part. The graph is interpreted by constructing equivalent circuits. Circuit elements characterize the electrochemical processes occurring in the cell. Such an approximation allows to extract the values of the parameters of each element of the chain to judge the nature of the ongoing processes (Fig. 4).

The specific ionic conductivity of the electrolyte is calculated by formula [28]:

$$\sigma = \frac{L}{R \cdot S},\tag{4}$$

where L is an electrolyte thickness, S is an electrolyte area, R is an ionic resistance of the electrolyte.

The transference number is calculated by formula [20]:

$$t^+ = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)},\tag{5}$$

where I_0 is an initial current during polarization, I_S is a steady current during polarization, R_0 is a charge transfer

resistance before polarization, R_S is a resistance charge transfer after polarization, ΔV is a magnitude of the applied polarization.

The maximum value of the transference number is 1. In most real electrolytes based on organic solvents, the salt usually does not completely dissociate resulting in ion pairs, triplets, and larger ion clusters formation. All of them can be mobile and promote charge transfer (Fig. 5). When conductivity is measured by applying a small alternating potential to an electrolyte, one takes into account the contribution of charge transfer from all charged mobile ions [29].

The most important feature that distinguishes an ion-conducting polymer from other ionic conductors is that polymer electrolytes are formed when salts with low lattice energy are dissolved (during dissolution, the lattice is destroyed and solvates or hydrates are formed) in a polar polymer matrix. For this reason, cations are responsible for direct current ionic conduction. In accordance with the theory of cation transport in high-molecular polymer electrolytes, cations are transported over long distances only in a dissociative way [27].

The potentiostatic intermittent titration technique (PITT) is a powerful technique to study the thermodynamic and transport properties of materials encountered in electrochemical processes. Because voltage and current can be controlled and measured precisely, PITT has become a commonly used electroanalytical method. Specifically, PITT has been used to measure the diffusion coefficient of solutes in host materials as well as to obtain quasi-equilibrium voltage–capacity profiles of battery electrodes after it was first developed by Wen et al. [30] to study LiAl alloys. Recently, PITT has been widely applied to characterize lithium diffusion in various LIB electrode materials, especially graphite negative electrodes and transition-metal oxide positive electrodes [31].

The galvanostatic intermittent titration technique (GITT) registers an equilibrium cycling curve; one can judge the kinetic properties of the system by the magnitude of the voltage deviation from the equilibrium value achieved after relaxation, when the current is applied. In GITT, small current pulses and register changes in potential. The imposition of a current pulse is accompanied by intercalation (deintercalation) of alkali metal ions into the electrode material, which deviates the system from equilibrium. Noteworthy, the small deviation of the system from equilibrium, therefore, a single titrated pulse should not lead to a significant change in stoichiometry of the electrode materials. This is followed by switching off the applied current and prolonged relaxation, during which the electrode must reach the equilibrium value of the potential corresponding to the new composition after the intercalation of a small number of alkaline ions [32].
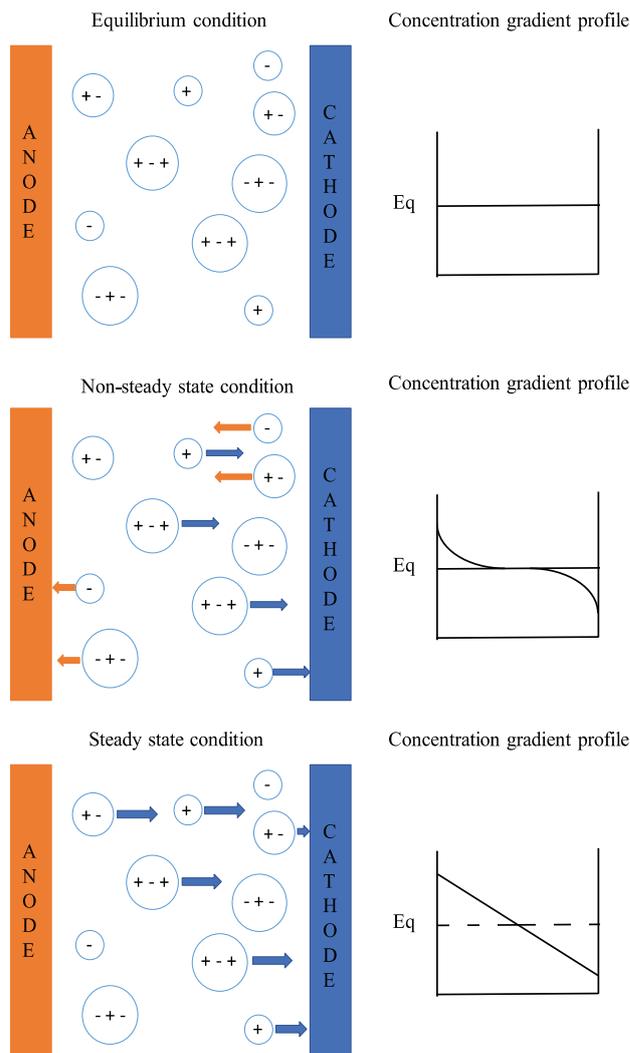

Fig. 5. Transport of the ionic species through the electrolyte and the concentration profile at equilibrium, non-steady state and steady state conditions. Adapted from Ref. [28].

The chemical diffusion coefficient D can be calculated at each step, with the following formula [30]:

$$D = \frac{4}{\pi}\left(\frac{iV_r}{Z_a FS}\right)^2\left[\frac{dE}{d\delta}\middle/\frac{dE}{d\sqrt{t}}\right]^2,\qquad(6)$$

where I (A) is the electric current; V_r (cm³/mol) is the molar volume of the electrode; Z_a is the charge number; F (96485 C/mol) is the Faraday's constant and S (cm²) is the electrode area. Besides, $dE/d\delta$ is the slope of the coulometric titration curve, found by plotting the steady state voltages E (V) measured after each titration step δ and $dE/d\sqrt{t}$ is the slope of the linearized plot of the potential E (V) during the current pulse of duration t (s).

Nowadays, in-situ/operando characterization becomes one of the most powerful as well as available means to monitor intricate reactions and investigate energy-storage mechanisms within advanced batteries, where "in-situ"

means "in the original place" and "operando" refers to "acting like in the natural state". Compared with traditional ex-situ techniques, in-situ/operando characterization can not only trace the electrode changes and complete reactions in real time, but also realize the detection of some sensitive electrochemical systems.

Because of its convenience and applicability, in-situ/operando X-ray diffraction (XRD) has burgeoned into a popular and powerful method in unravelling phase transitions within various electrode compounds. While in-situ nuclear magnetic resonance (NMR) is capable of capturing the atomic structure, local environment and dynamic information during charge/discharge progress. In-situ transmission electron microscopy (TEM) also plays an important role in studying the phase transformation and interfacial property due to its superior resolution. Through non-invasive characterizations, the information about real-life evolution of electrode structures could be collected under operando conditions. The electrode/electrolyte interface or the electrode surface is the most crucial region in battery studies, where complicated reactions occur, including the formation of solid electrolyte interface (SEI), the redox reactions of functional ions and other side reactions. The in-situ TEM can be utilized in probing the interfacial structure changes during the cycling. Along with component variation, the structure evolution is of great importance in understanding the charge-storage mechanism of electrode materials, especially for layered-oxide cathodes, which needs in-situ recording of the changes of the microstructure and phase transition.

Furthermore, some other in-situ techniques make much contribution to the surface/interface morphology research, such as optical microscopy, atomic force microscopy and scanning electron microscopy. Apart from the topographic information, the investigation of surface electrochemical properties has been attained through different in-situ measurements, including synchrotron X-ray absorption spectroscopy (XAS), Raman spectroscopy and scanning electrochemical microscopy (SECM). XAS is widely adopted in probing the local atomic arrangement and electronic structure of material surface, and Raman is adept in detecting the surface compounds, especially intermediate products. While SECM provides spatially resolved messages about interfacial electrochemical activity [33].

4. MATERIALS FOR CATHODE, ANODE AND ELECTROLYTE

4.1. Cathode materials

Among various cathode materials, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC811) has attracted much research interest due to its high theoretical capacity (~280 mA·h/g), high energy density (~800 W·h/kg) and low cost. However, wide practical use of this material is challenging. For example, in layered cathode materials, Li^+ and Ni^{2+} cations mix during the lithiation/delithiation process due to the similar ionic radius, this leads to a decrease in capacity and causes destruction of the material surface, leading to irreversible phase transformation [34]. The NMC532 possess the optimized composition to maintain a reasonably good thermal stability, comparable to the low-nickel-content materials (e.g., NMC333 and NMC433), while having a high capacity close to the high-nickel-content materials (e.g., NMC811 and NMC622) [35]. Ethical concerns should be raised about the use of cobalt, since 70% of this element is found in only one country: the Democratic Republic of the Congo (DRC). About 90% of the cobalt in the DRC comes from industrial mines, but because of the low economic level of the population, the global demand for cobalt has attracted thousands of individuals and small businesses, and child labor and unsafe work practices are widespread. Chemists are exploring ways to replace cobalt with more common metals such as iron or manganese [36].

Composites based on $LiFePO_4$ are used as electrode materials due to their environmental friendliness, low toxicity [37], and low price. However, the application of $LiFePO_4$ is limited because of its low performance and low capacity (170 mA·h/g), which results in significant power loss with increasing current density [5]. Among the approaches used to modify cathode materials based on $LiFePO_4$, one should note the use of nanomaterials, the substitution of a part of iron ions, and the formation of composite materials with conductive additives. Because charge transfer typically occurs much faster in the intergrain space than in crystals, reducing the particle size and decreasing the diffusion path length significantly increases the charge/discharge rate. To reduce the migration path of Li^+ inside the particles, there is no need to reduce their size in all directions, because the diffusion of Li^+ occurs along one direction [5]. Various forms of carbon are used as additives, such as amorphous carbon, graphite, graphene, and carbon nanotubes. Making composites with carbon does not only increase conductivity, but also prevents particles from sintering during annealing resulting in a finer material. A thin carbon layer provides accelerated electron transport to the $LiFePO_4$ surface without blocking the transfer of lithium cations. In the case of using polyvinylidene fluoride (PVDF) as a carbon source, the carbon coating layer can be accompanied by simultaneous doping of $LiFePO_4$ particles with fluorine ions, which can enhance the electrochemical performance of materials based on $LiFePO_4$ [37].

Various cathode materials have been used in LIBs, such as $LiCoO_2$ (LCO), $LiFePO_4$, $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), nickel-rich layered oxides, lithium-rich layered
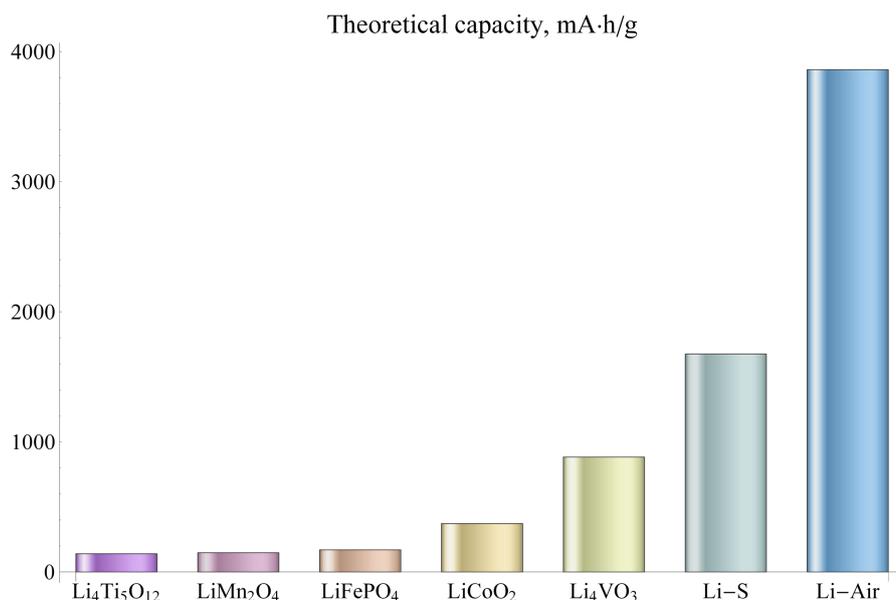
Theoretical capacity, mA·h/g

Fig. 6. Theoretical capacity of various cathode materials for rechargeable lithium batteries.

oxides (LLO), etc. [38]. Despite the fact that LCO has a good compaction density ($\sim$4.2 g/cm^3) and a high operating voltage ($\sim$3.9 V), which provide it with a high volumetric energy density: the scarcity, high cost, and toxicity of cobalt hinder the widespread use of such materials. Low-cobalt or cobalt-free cathode materials are currently being developed, and LCO is gradually being replaced by industrial cathode materials such as LiFePO$_4$, LiMn$_2$O$_4$ and nickel-rich layered oxides, as well as near-commercial cathode materials such as LLO and LNMO [39].

Usually, the introduction of lithium ions into the material of a positive electrode is accompanied by a change in the valency of one element of the material. In lithiated cobalt and iron oxides, the maximum change in valence is a unit. In vanadium oxide, the valency of vanadium can vary by 3 units, i.e., in Li$_4$VO$_3$ (this is stoichiometrically equivalent to Li$_2$O·Li$_6$V$_2$O$_5$), 6 lithium ions are inserted per formula unit V$_2$O$_5$). In this case, the specific capacity is 883 mA·h/g [40]. The graph (Fig. 6) shows the theoretical capacity of cathode materials for a lithium battery.

Recently, lithium-air batteries have been considered as a possible replacement for LIBs because their theoretical capacity is much higher. Although this has stimulated intensive research and commercial interest, such a battery has its own problems: electrolyte instability, low rate capability, low efficiency and limited life. Ref. [41] describes lithium-air battery configuration using lithium metal as the negative electrode, a porous high surface area material (e.g., carbon) as the positive electrode, and oxygen as the active material. Instead of graphite anode used in LIB directly lithium metal can be used as an anode in the lithium-air battery which enhanced Li-air battery capacity 10 times higher than that of conventional LIB. Also,

oxygen from the air can be absorbed freely into the cathode of LIB leading to a huge reduction in the weight and the cost of the battery [42]. During discharge, oxygen is reduced and forms superoxide radical anions, which can combine with lithium ions and result in a superoxide (LiO$_2$) to form the desired discharge product, lithium peroxide (Li$_2$O$_2$). These types of superoxide and peroxide readily degrade carbonate-based electrolytes such as ethylene and propylene carbonate. For the stable operation of lithium-air batteries, it is important to choose the right electrolyte. The use of solid state electrolytes in lithium-air batteries can solve this problem. Of the polymers studied, poly(acrylonitrile) (PAN) appears to be the most reactive with Li$_2$O$_2$, while poly(vinylpyrrolidone) (PVP) the least. The halogenated polymers have similar reactivities, although at longer times, PVDF appears more reactive than poly(vinyl chloride) (PVC) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [41].

With an ultra-high energy density of 2600 W·h/kg, combined with non-toxicity and environmental friendliness, lithium-sulfur batteries appear to be the most promising energy storage systems. However, their large-scale application and commercialization are hindered by the low electronic conductivity of sulfur and Li$_2$S, the shuttle effect of intermediate lithium polysulfides (LiPS), the volumetric expansion of sulfur (80%) after lithiation as well as the formation of lithium dendrites. In Ref. [43] the improvement in the performance of a sulfur cathode was demonstrated by incorporating metal nanoparticles into nanostructured carbon materials. Wang et al. [44] reported on high-dispersity Co nanoparticles on nitrogen-doped layered porous ultrathin carbon nanosheets; the Co nanoparticles exhibit a strong chemical interaction with sulfur

in polysulfides. The polar Co components can catalyze conversion reactions in LiPS resulting in high reversible specific capacity and long cycle stability when using sulfur cathodes for lithium-sulfur batteries: the specific discharge capacities was 1505 mA·h/g for 0.1 C, the Coulomb efficiency is over 96% after 300 cycles [44].

Given the capacity limitations of oxide cathodes with an insertion reaction, cathodes with a conversion reaction, such as sulfur and oxygen, are an alternative. However, this type of battery, both lithium-sulphur and lithium-oxygen batteries have problems limiting their commercial application.

4.2. Anode materials

4.2.1. Classification

There are three main types of anode material for LIB: intercalation, conversion and alloying types. The reaction mechanism for intercalation-type anode materials is based on the intercalation and deintercalation of lithium ions in the crystal lattice of the host material. As a layered carbon material, graphite was the first commercialized LIB anode material. Layered LiC_6 can be formed by intercalating lithium ions. The discharge plateau of LiC_6 is below 0.2 V (vs. Li^+/Li) and it has outstanding dynamic performance for the intercalation of lithium. However, because of the slow diffusion rate of lithium ions, the rate performance of graphite is not ideal. The intercalated lithium potential is similar to the stripping potential of lithium metal and therefore lithium dendrites and solid electrolyte interphase (SEI) films can easily form [45].

Conversion-type anode materials (CTAMs) mainly refer to transition metal oxides, sulfides, phosphides and nitrogen compounds (Me = Co, Ni, Fe, Mn). The transformation reaction of metal oxides and sulfides with Li^+ is as follows:

$$Me_xO_y + 2yLi^+ + 2ye^- \leftrightarrow xMe + yLi_2O,$$

$$Me_xS_y + 2yLi^+ + 2ye^- \leftrightarrow xMe + yLi_2S.$$
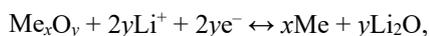
Because there is no position for Li^+ insertion and extraction in the spatial structure of CTAMs, it is generally believed that the reaction with Li at room temperature is irreversible. CTAMs possess some advantages, such as composition diversity and high theoretical capacity. For the broad class of conversion materials, the conversion redox reactions ultimately result in the formation of the metallic phase. The major issues that need to be addressed if the conversion materials are to invoke a potential commercialization claim are voltage hysteresis, long sloping regions in discharge profile (voltage-dependent redox reaction), inconsistent cycling stability, rate instability, and higher first-cycle capacity loss. Various underlying

phenomena can be associated with these adversities, three of which need a mention here. They are: irreversible electrolyte decomposition, incomplete back conversions, and the back conversion to the phases that can permit less Li/Na uptake than the original one [46].

Methods for improving the performance of conversion anodes: particle size control, morphological control, composition control and composite with carbon. Particle size has a huge impact on the overall electrochemical performance. Some comparative studies on the effect of particle size have revealed a better performance of nanosized particles than micron-sized particles. This better performance is due to shortening of insertion path length that Li has to traverse. Utilization of the bulk of the material upon nanostructuring leads to considerable capacity enhancements. Ultrasmall nanoparticles, nanoneedles, nanorods, nanospindles, nanosheets, and other nanoscale architectures have resulted in the enhancement of capacity by the complete utilization of material, harnessing the benefits associated with the nanomorphologies in general [47]. Composition has a marked influence on the overall performance of material. Different transition-metal compounds with different anion species with formula Me_aX_b, where X = F, O, S, P, and H, have been shown to exhibit Li/Na insertion by reversible conversion reaction with a theoretical capacity that is by a factor of three higher than that of commercial graphite. Among different conversion anodes, transition-metal oxides are the most explored, which include both binary and ternary oxides of 3d transition metals, such as Cr, Mn, Fe, Co, Ni, and Cu. Various phases of different binary oxides of 3d transition metals, including Cr, Mn, Fe, Co, and Ni, and 4d transition metals, including Nb and Mo, have been studied for their suitability as negative electrode in LIB. Carbon-based composites seem to be more promising as they possess high electrical conductivity, high surface area, and good mechanical strength. In addition to improving the high current performance by reducing the electronic resistance, the carbon support absorbs the strain due to the volume expansion in the electrode which renders better cyclic stability.

Alloyed anode materials primarily belong to the IV and V groups, which include Si, Ge, Sn, Pb, P, As, Sb and Bi. The lithium storage mechanism is an alloying reaction with lithium to form a Li_xM alloy. The corresponding alloying reaction, taking Si as an example, is as follows:

$$Si + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Si.$$

Due to the atoms of any alloy-type material theoretically holding 4.4 or 3 Li^+, they exhibit very high specific capacities, for example, silicon (4200 mA·h/g). It has the highest theoretical capacity of any anode material, however, the volume changes greatly during the lithiation reaction, resulting in the formation of a significant outward

stress inside the material, which causes the electrode material to be crushed and separated from the collector in serious cases. The SEI film also ruptures, exposing a new surface and requiring the continued consumption of lithium to reform the SEI film. Thus, the cycling performance is relatively low [45].

4.2.2. Existing and promising materials

The use of carbon as an anode material for Li-ion continues to this day due to its low cost and high cyclic stability; however, its low capacity (372 mA·h/g) cannot meet the requirements of electronic devices and electric vehicles [41]. Lithium intercalation into carbon materials is a complex process, its mechanism and kinetics largely depend on the nature of the carbon material and electrolyte. An obligatory condition for the normal functioning of LIB, which uses graphite as an anode, is the formation of a passivating layer on its surface from the products of the reduction of electrolyte components. Decomposition of the electrolyte leads to the formation of a surface protective film, which ensures the continuous operation of carbonized anodes. On the other hand, the formation of this film is accompanied by some irreversible initial capacitance, resulting in the release of gaseous products, which is extremely undesirable for operation and from the point of view of cell safety [8].

The electrical conductivity of an electrode is influenced by the surface area of the electrode particles; the interaction of ions and electrode particles in redox is increased in an electrode with a large surface area. As a result, it increases the number of electrons flowed by electrodes or increases the electric current. One method to increase the electrical conductivity is increasing the surface area of the electrode particles by making the particles small (nano/microparticles); the rearrangement of these particles results in a larger surface area. Conductivity is also influenced by porosity, which influences the extent to which ions can enter between particles [48].

Electrode materials derived from biomaterials are of great interest due to their high carbon content, low cost, and environmental friendliness. For example, in Ref. [49] champignons were used as an anode material without the use of harmful solvents or chemical activation agents. These new anodes contain no binder or conductive additives while achieving comparable performance to graphite-based electrodes. A common microstructural feature of this material is nanobelts about 10 μm wide, several tens of microns long, and about 20–100 nm thick. The specific discharge capacity of this anode is 289 mA·h/g.

Both silicon and germanium form alloys with a high lithium content, with the composition $Li_{22}X_5$ (X = Si or Ge). Such alloys can be produced by electrochemical

incorporation of lithium into Si and Ge electrodes, which makes them very attractive as anode materials for lithium-ion batteries. The theoretical capacity of Si is about 4000 mA·h/g and 1300 mA·h/g for Ge [50]. Although Ge shows a lower specific capacity, the electronic conductivity and diffusion coefficient of Li in it are almost two orders of magnitude higher than that of Si. This allows considering Ge as an anode material suitable for a high power battery, although the cost of Ge is quite high. However, during cycling, a volume expansion of 300–400% occurs, which leads to the destruction of the electrode and a decrease in capacity. As quality solutions to these problems, in Ref. [50] it was proposed the use of a variety of nanostructured materials, including nanowires and nanoparticles, which can withstand large material expansion/contraction during cycling. Carbon nanowalls (CNWs) obtained by the methods of chemical vapor deposition, plasma enhanced chemicals vapor deposition were used as scaffolds for fabrication of multilayer composite electrodes based on Si and Ge. The above-mentioned approach enabled fabrication of the electrodes with specific capacities that retained at the level of about 2900 mA·h/g for Si (70% of theoretical capacity) and 1400 mA·h/g for Ge (80% of theoretical capacity) after 100 cycles. The capacities calculated taking the CNW weight into account were 465 and 440 mA·h/g for Si- and Ge-based electrodes, respectively, which are higher than those for commercial graphite. Scanning electron microscopy analysis of the electrodes suggests that the improved cyclic stability of Si/Ge/CNW multilayer electrodes is provided by efficient mechanical stress relaxation within these films.

Humana et al. [51] attempted to solve the problem of silicon-based anode destruction by creating silicon/graphene composite materials. The change in the morphology of silicon nanoparticles — the transition to whiskers (filamentous crystals) — made it possible to increase the capacity to 1600 mA·h/g for 100 charge/discharge cycles [52]. Also, SiO_2 nanoparticles can effectively etch lithium dendrites and slow their further growth through the solid-state transformation reaction.

Tin has a specific capacity of 991 mA·h/g, which makes this metal a very promising anode material [53,54]. In Ref. [55] SnO_2 nanowires were synthesized by the thermal evaporation of metallic Sn on the basis of an Au vapor-liquid catalyst. The first capacity is 2133 mA·h/g, which is much larger than the theoretical capacity of bulk SnO_2. Carbon in SnO_2 nanowires can accumulate lithium, but its possibilities are very limited. It has been shown that SnO_2 nanowires can relieve stresses associated with lower volume change due to the formation of nanocrystalline particles.

Transition metal sulfides (TMSs) have attracted significant interest as energy storage materials for high-

performance supercapacitors, LIBs, and fuel cells [56]. Cobalt sulfides are one of the most widely studied TMSs due to their high capacity, controllable structure, and rich variety of stoichiometric compositions such as CoS, CoS_2, Co_3S_4, and Co_9S_8. However, the primary challenges faced by cobalt sulfide-based electrodes can be divided into the categories of significant volume expansion, low conductivity and dissolution of the polysulfide in organic electrolytes. To solve problems, TMSs uses the design of hollow nanostructures. It is believed that the hollow inner can provide a void space which can accommodate the volume expansion of metal sulfides and improve the Li^+ access by decreasing the ion diffusion path length [57]. Conductive coatings or nanocomposites with different nanocarbon can be utilized to increase the conductivity of cobalt sulfides, and enhance the electrochemical performance [58]. Recently, a MoS_2 LIB anode characterized by the open structure with large interlayer spacing and high specific capacity ($\sim$ 673 mA·h/g) has been developed [59].

4.2.3. Addition of transition metal oxide nanoparticles to a graphite electrode

The way to develop electrodes with a higher capacity is to pack as many Li^+ ions as possible into electrodes so that the electrochemical reaction could include a higher stoichiometric Li^+ ratio during charging and discharging. As a promising alternative to commercial electrodes, metal oxides have long been studied as potential electrode materials for LIBs [22]. The main problem of electrode materials is that their structure is destroyed in the process of charging and discharging, which leads to the failure of a lithium-ion battery. Another important problem is a formation of irreversible Li_2O at first cycle, that leads to the consumption of lithium from the cathode material. It should be noted the whole amount of lithium is in the cathode, and in the case of using not intercalation type of anode, much more lithium is wasted. The use of nanoparticles of transition metal oxides can improve the capacitive characteristics due to a larger surface of the active mass of substance. Moreover, it tends to increase the number of recharge cycles due to the mechanical properties of the nanoparticles [60]. The transition to nanoscale materials also makes it possible to enhance battery charging rates due to a decrease in the Li^+ diffusion path and an increase in the electrode/electrolyte interface surface area [61].

Due to their promising potential, metal oxide anodes, including their nanostructures and composites, have been extensively researched. Among various metal oxides, copper oxide (CuO) stands out [62–64], because it is a common element, environmentally friendly, and inexpensive. The maximum reversible capacity is 674 mA·h/g. However, a decrease in CuO capacity results from volume changes (174%), weak electrical conductivity and morphological transformation because of mechanical aggregation during lithium incorporation and extraction [65]. In Ref. [66], CuO showed a reversible capacity 2–3 times higher that of commercial graphite anode material and a cyclic performance higher than that of nanosized SnO_2.

The binder used in anodes also has an effect on the performance of the battery. After 100 charge-discharge cycles, the CuO electrode containing carbomethylcellulose (CMC) maintains a stable capacity of at least 200 mA·h/g, and in the electrode with PVDF, the capacity drops to 60 mA·h/g. Presumably, CMC has better adhesion to the surface of Cu_2O/CuO nanowhiskers, adapting to the volume expansion of the anode during cycling [67].

Ref. [61] presents an anode for lithium-ion batteries based on CuO, in which CuO nanofibers directly grow on a copper substrate. The main advantage of this electrode is that it avoids complex fabrication procedures (e.g., the use of a polymeric binder and conductive agent), it also allows to create a better electrical contact between the current collector and the active material and increase the energy density of the electrode. Moreover, the characteristics of CuO nanostructures can be controlled by the synthesis conditions. The initial discharge capacity of the resulting electrode is about 970 mA·h/g, which is more than the theoretical value.

ZnO as a representative of transition metal oxides is widely studied in the field of optics, electronics, semiconductors, molecular devices, etc., due to its availability, low cost, and environmental friendliness. Although ZnO has a theoretical capacity of 987 mA·h/g as an anode material for lithium-ion batteries, it exhibits a lower reversible capacity and poorer cyclability compared to other transition metal oxides because of low electronic conductivity and large volume change of ZnO particles during the discharge/charge process [68].

Titanium oxides with one-dimensional nanostructures are of particular importance as their unique morphology provides a large specific surface area. There are methods for preparing nanostructured TiO_2, for example, the treatment of TiO_2 powders in NaOH solution using aluminum oxide, as well as the sol-gel method [69]. The thickness of the TiO_2 nanorods obtained in Ref. [20] is several nanometers, which has a significant advantage, as it is comparable to the free path length of electrons and can easily diffuse into the electrode. The gradual introduction of lithium into anatase TiO_2 leads to an increase in the lithium titanate phase and a decrease in the fraction of the lithium anatase phase, while the lattice volume grows only by 3%. Notably, the reactivity of TiO_2 with lithium is higher than that of SiO_2, considering a better inhibitory effect on lithium dendrites. Moreover,
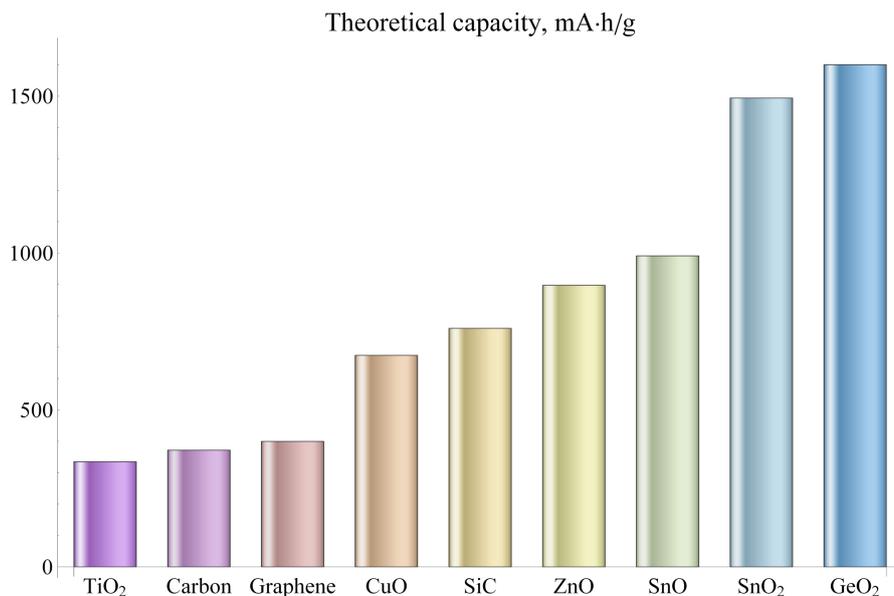
Theoretical capacity, mA·h/g

Fig. 7. Theoretical capacity of various anode materials for rechargeable lithium-ion batteries.

TiO_2, acting as an amphoteric oxide, can neutralize acidic substances in the electrolyte and reduce the loss of cathode materials [70].

One-dimensional nanostructures in the form of whiskers, tubes, rods, etc. better withstand the mechanical stresses arising during the lithiation/delithiation process [71,72], and provide a longer battery life.

Fig. 7 shows the theoretical capacity of materials used as additives in the anode of a lithium-ion battery.

In recent years, there has been a need for new anode materials that could serve as an alternative to traditional graphite anodes, the power of which does not meet modern requirements for high-performance lithium-ion batteries of a new generation. The aforementioned non-conventional anode materials can be divided into four main categories, namely, alloy materials, conversion-type transition metal compounds, silicon-based compounds, and carbon-based compounds. Each of the categories has promising characteristics, but also disadvantages that limit their performance. To solve these problems, researchers are using inert additives and developing composite anodes.

4.3. Electrolyte materials

Compared to the research dynamics in the field of electrode materials, advances in electrolytes occur more slowly, while maintaining the main composition: lithium salt and organic carbonate solvents. This can be explained by the fact that the electrolyte components (especially solvents) are extremely sensitive to the working potential but not to the capacity of electrodes; therefore, as long as new chemical materials operate within the electrochemical stability window of electrolytes, no major changes in electrolyte composition occur. Liquid organic electrolytes have high ionic conductivity. This is a key property of the electrolyte, since ionic conductivity quantifies how mobile (and available) the ions are for the current electrochemical reaction, which partly determines the power of the cell [73].

Liquid electrolytes are usually obtained by dissolving a lithium salt in an organic solvent, they have high ionic conductivity (about $(1–10)\cdot10^{-3}$ S/cm) and good contact with the electrode. However, the safety of liquid electrolytes is limited, and the lithium metal anode cannot be used in liquid electrolyte systems because of the growth of lithium dendrites, which limits the energy density of batteries. When liquid electrolytes are heated, the pressure of saturated vapors of low-boiling aprotic solvents increases (Table 1), which leads to side reactions with the release of gaseous products. Commonly used organic solvents for electrolytes include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and their

Table 1. Melting and boiling points of some organic solvents.

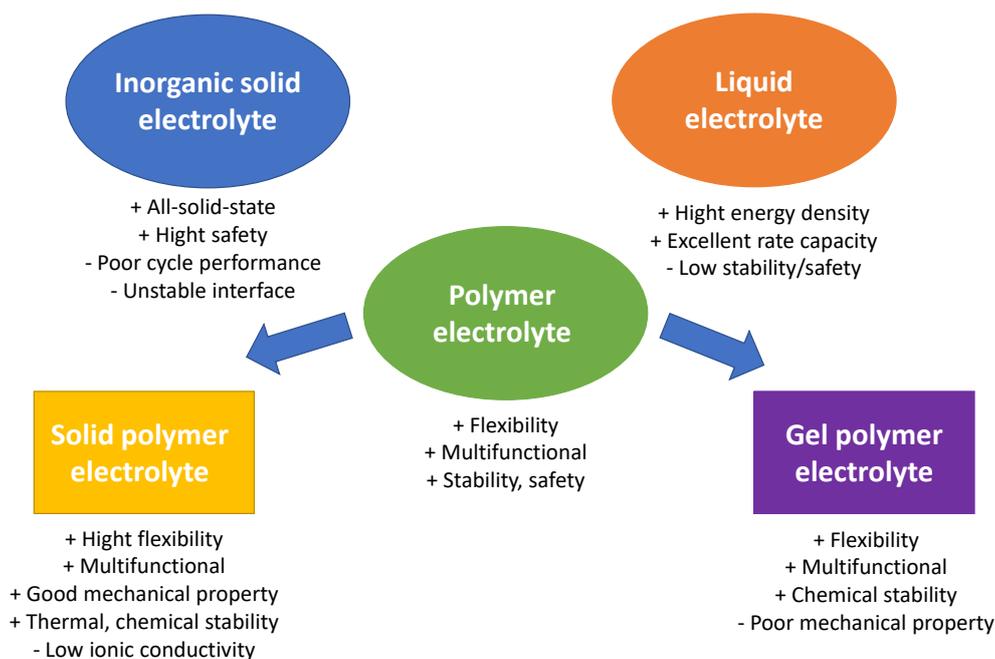| Solvent	Melting temperature, °C	Boiling temperature, °C
ethylene carbonate, EC	39	248
propylene carbonate, PC	−49	240
dimethyl carbonate, DMC	4	90
methylethylene carbonate, MEC	−55	109
diethyl carbonate, DEC	−43	126
1,3-dioxolane, DOL	−95	75
1,2-dimethoxyethane, DME	−58	84

Fig. 8. Types of electrolytes, their advantages and disadvantages.

mixtures, however, they are generally flammable and inflammable [74].

The safety of the battery can be increased by replacing liquid electrolytes consisting of organic flammable components with a much less flammable polymer. Another advantage of the gel-polymer electrolyte (GPE) is flexibility and elasticity, as well as the ability to tolerate changes in the volume of electrode materials. Fig. 8 shows the currently existing types of electrolytes, as well as their advantages and disadvantages.

The transition from liquid to polymer electrolytes was proposed in 1978 [75] when polyethylene oxide (PEO) was doped with lithium salts. Unfortunately, the first generation polymer electrolytes had very low room temperature conductivity [76]. High crystallinity of PEO at room temperature prevents the movement of chain segments, and PEO ionic diffusion capability are not ideal. Many other types of polymers have been developed as the basis of electrolytes, such as PAN [77], PC [78], polymethyl methacrylate (PMMA) [76,79,80], PVDF [13,74], and PVDF-HFP [81–83]. Among them, PVDF and PVDF-HFP materials are very promising as solid electrolytes for lithium batteries due to their higher dielectric constant, chemical stability, and higher mechanical strength [74]. Also, it is important to take into account the thermostable properties of polymers (Table 2).

Polymer electrolytes contain both crystalline and amorphous regions, it is known that ion transport occurs mainly in the amorphous region. Applying plasticizer solvents, the amorphous region can be enlarged to enhance the electrical conductivity of the electrolytes [29]. The

polarity of the polymer greatly influences the interaction between ions, for example, PVDF has a high relative permittivity of 8.3, while the dielectric constant of PEO is only 5. PVDF has ideal properties as a solid electrolyte: mechanical strength, thermal and chemical stability, incombustibility [74]. However, the presence of a strong polar C–F bond degrades the compatibility between PVDF and lithium, resulting in an increase in interfacial resistance. Therefore, researchers are focusing on obtaining a new polymer electrolyte by mixing different polymers, and synthesizing composite polymer electrolytes with the addition of inorganic fillers.

4.3.1. Gel-polymer electrolytes

The use of well-designed copolymers is a method to improve battery performance. Yuan et al. [7] developed a polymer electrolyte based on a copolymer of polyvinyl

Table 2. Melting and decomposition points of some polymers.

Polymer	Melting temperature, °C	Decomposition temperature, °C
polyethylene oxide, PEO	65	243
polyacrylonitrile, PAN	317	280
polymethyl methacrylate, PMMA	125	270
polyvinyl chloride, PVC	150	110
polyvinylidene fluoride, PVDF	177	382
poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP	114	330

chloride and polyacrylic acid PVC/PAA. PAA has high mechanical strength, in addition, there are many polar groups on PAA polymer chains, where the effective distance between carboxyl groups (–COOH) can be controlled by copolymerization with other monomers. The proton on the carboxyl groups was replaced by a lithium ion, which increased the content of lithium ions in the electrolyte and improved the affinity for the electrolyte. The resulting GPEs do not only show high tensile strength and elongation, but also stabilize the Li metal anode due to a more uniform and faster Li-ion transport.

In Ref. [12], PMMA polymer was added to PVDF, which led to a decrease in crystallinity. Luo et al. [83] demonstrated that the crystallinity of GPE reduces, when PVDF is copolymerized with HFP, the affinity for liquid electrolyte and the electrochemical stability are better compared to pure PVDF GPE. They also described a method for forming an interpenetrating polymer (IPN), which is a semi-interpenetrating network consisting of a crosslinked and a linear polymers. This can not only reduce crystallinity, but also improve the compatibility of immiscible phases. Yao et al. compared a gel-electrolyte based on PVDF and dimethylformamide (DMF) at different drying temperatures [84]. The electrolytes dried at 60 °C contained 23% DMF and had an ionic conductivity of $0.12 \cdot 10^{-3}$ S/cm at room temperature. When the drying temperature was raised to 80 °C and 100 °C, the DMF content was only 6.3% and 3.3%, while the ionic conductivity decreased by two orders of magnitude. These results suggest that the solvent content has a critical effect on the ionic conductivity of GPE.

While most previous research has tended to suggest that cyclic carbonate molecules (EC, PC) are preferred due to their higher dielectric constant and dipole moment, others have argued that this preferred solvation (electrostatic interaction between particle ions, solute molecules substance and solvent) does not exist. Using nuclear magnetic resonance Matsubara et al. [85] compared several solvents and determined that Li^+ solvation does occur and the relative competitiveness of each solvent with respect to penetration into the Li^+ primary solvation shell appears to be related to their density rather than their dielectric constant. The research results [86] confirmed that cyclic carbonate solvents are preferred for the primary solvate shell of Li^+, while neither the types of salts nor their concentrations have a significant effect on this trend.

Compared to PAN-based GPE, PMMA-based GPE has better interfaces with respect to lithium electrodes, however, it has weak mechanical properties. Plasticized PMMA-based polymer electrolytes are more conductive than a plasticizer-free sample. Ionic conductivity peaks at $1.28 \cdot 10^{-4}$ S/cm for $PMMA/LiN(SO_2CF_3)_2/EC$ (weight composition 80% (85% PMMA + 15% $LiN(SO_2CF_3)_2$) : 20% EC) and $2 \cdot 10^{-4}$ S/cm for $PMMA/LiN(CF_3SO_2)_2/EC/PC$ (weight composition 70% [80% (85% PMMA + 15% $LiN(CF_3SO_2)_2$) + 20% EC] : 30% PC). This indicates that the physicochemical properties of individual plasticizers, such as high dielectric constant EC ($\varepsilon = 85.1$), PC ($\varepsilon = 69.0$) and low freezing point PC (−49 °C) significantly contribute to the improvement of conductivity characteristics. The addition of a plasticizer also reduces the chance of ion pairing. The high dielectric constant of EC effectively reduces the interionic Coulomb interactions, which leads to an increase in the conductivity of Li^+. In addition, the mixture of EC and PC has a dielectric constant of 87.2 at 25 °C, which is higher than either alone [60].

Being a thermoplastic polymer, PMMA acts as a scaffold for the gel electrolyte. When PMMA is added in excess of ~20 wt.%, liquid electrolytes completely transform into a gel. With further addition of PMMA, the electrolyte hardness increases, which leads to a decrease in conductivity. In addition, an important observation was recorded — the electrical conductivity of GPE containing PMMA (up to 10 wt.%) is slightly higher than that of liquid electrolytes without PMMA. The movement of polymer chains leads to local vibrations, and this leads to further dissociation of ion pairs and an increase in ion mobility, resulting in higher conductivity [79].

Ionic liquids are other promising area. In Ref. [87], a GPE was synthesized containing the ionic liquid 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfnyl)imide (EMITFSI). The addition of EMITFSI to the PVDF-HFP-LiTFSI polymer electrolyte improves the ionic conductivity to $2.11 \cdot 10^{-3}$ S/cm, while the electrochemical window is 4.6 V. The high temperature of 80 °C do not significantly affect the battery cycling.

The great advantage of GPE is that it combines the characteristics of a polymer matrix (mechanical stability, flexibility) with excellent ionic conductivity close to that of liquid electrolytes. The following polymers are most widely used in the manufacture of GPE: PEO, PMMA, PAN, PVDF/PVDF-HFP. Moreover, due to their unique advantages, these GPEs are also promising for flexible and wearable electronic devices. Currently, many attempts are being made to develop new GPEs and improve their performance, for example, by forming composites, which will be discussed below.

4.3.2. Metal oxide nanoparticles in GPE

An inorganic filler typically includes inert materials (e.g., TiO_2, SiO_2, Al_2O_3, etc., which are non-ionic conductive fillers) and active fast ionic conductors (e.g., LATP (lithium aluminium titanium phosphate) and LLZTO (lithium lanthanum zirconium tantalum oxide),

also known as conductive ceramics). They can interact with lithium ions and polymers, reducing the crystallization of polymers and increasing the movement of chain segments, which contributes to better diffusion of lithium ions. These inorganic materials have high hardness, forming a composite system that can improve the polymer mechanical properties. It is useful for inhibiting the growth of lithium dendrites [52,88] and preventing damage to electrolytes during manufacturing and assembly. In Ref. [84] palygorskite ($(Mg,Al)_2Si_4O_{10}(OH)$) nanowires (50 nm in diameter and ~1 μm in length) were added to GPE, which significantly increased the elastic modulus (from 9 MPa to 96 MPa) and yield strength (from 1.5 MPa to 4.7 MPa), which contributed to the inhibition of dendritic growth. The Li-ion transference number increased from 0.21 to 0.54, which means an improvement in cycle performance. Batteries assembled from this electrolyte with $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode and lithium anode could be cycled more than 200 times with 97% capacity retention. The cycling protocol was 0.1 C for three cycles, followed by 0.3 C between 4.2 and 3.0 V. The specific capacity remains at 118.1 mA·h/g after 200 cycles.

The addition of an inorganic filler affects the mechanical and electrical properties of electrolytes; however, it is important to consider their concentration. Several works consider the influence of the concentration of an inorganic filler.

Dorogov et al. [89] studied the effect of the concentration of CuO nanoparticles (< 50 nm) in a PVDF-based electrolyte on battery performance. Specific ionic conductivity for a sample containing 0.1 wt.% CuO nanoparticles was $5.85 \cdot 10^{-3}$ S/cm, which is a high conductivity comparable to that of liquid electrolytes. Batteries with an electrolyte containing a high concentration of nanoparticles quickly failed, probably because of electronic breakdown between the electrodes. It was shown that the concentration of copper oxide nanoparticles in the electrolyte does not significantly affect the ionic conductivity, but affects the service life (increases the number of charge/discharge cycles while maintaining the capacity level).

The article [90] describes the preparation and characterization of a nanocomposite polymer electrolyte based on PVDF-HFP with SiO_2 nanoparticles (12 nm with surface area of 200 m^2/g) as a filler. The electrolyte with 2.5 wt.% SiO_2 showed a conductivity of $1.16 \cdot 10^{-3}$ S/cm at ambient temperature. It was found that a filler content of more than 2.5 wt.% lowers the conductivity of the electrolyte. This suggests that the movement of molecules in composite polymer systems is hindered above a certain filler concentration. A higher viscosity of the polymer medium leads to a decrease in ion mobility, which leads to a decrease in conductivity. The increase in viscosity can be

attributed to the strong interaction between the particles of the filler and the polymer matrix, which slows segmental movement of the polymer chain.

The electrolyte based on PVDF/PVC and LiBOB salt was doped with ZrO_2 (20–30 nm with surface area of 35–45 m^2/g). A mixture of composite polymer electrolytes was prepared using the method of casting from a solution with a change in the concentration of the filler. The maximum conductivity of $4.38 \cdot 10^{-4}$ S/cm was obtained with a filler content of 2.5 wt.%. A further increase in the filler content tends to decrease the conductivity. This may be due to the aggregation of nanoparticles, which strongly interact with polymer chains. A slight improvement in conductivity was observed above 7.5 wt.%. An increase in ionic conductivity occurs due to a decrease in the crystalline phase of the polymer; therefore, the ionic conductivity of the polymer electrolyte can be improved by increasing the amount of lithium ions. The activation energy of ion transfer is maximum for electrolytes without a filler and increases from 2.5 to 7.5 wt.% and again decreases by 10 wt.% [91].

TiO_2 effectively affects the crystallinity of PVDF by lowering the glass transition temperature, thereby increasing miscibility and improving mechanical stability. However, studies have shown that an excess content of TiO_2 leads to phase separation and a decrease in the conductivity of the lithium ion [92]. In Ref. [93] it was found that $AlPO_4$ nanoparticles have the ability to increase the amount of transported Li^+ ions and stabilize the electrode-electrolyte interface. The addition of TiO_2 nanoparticles to the PVDF/HFP polymer matrix together with polyphenylene isophthalamide nanofibers leads to an increase in ionic conductivity and electrochemical stability of the lithium-sulfur battery due to the prevention of the formation of lithium dendrites and the transfer of sulfur compounds [94].

Chitin, which is the most abundant biopolymer after cellulose, has low toxicity, biodegradability, and antibacterial activity. Stefan et al. [95] used nanochitin as a new inert filler in the $PEO-LiPF_6$ electrolyte. Incorporation of chitin enhances the ionic conductivity up to one order of magnitude. The tensile strength of the polymeric film was increased from 1.9 MPa (89% PEO + 5% $LiPF_6$) to 2.6 MPa (85% PEO + 10% chitin + 5% $LiPF_6$). Further addition of chitin also increases its modulus value from 2.6 MPa to 3.3 MPa (75% PEO + 20% chitin + 5% $LiPF_6$). However, the total elongation to failure decreased from 22% (without chitin) to 12% (20% chitin) and maximum elongation to failure (~30%) was observed in sample with 10 wt.% chitin. However, at higher concentrations of chitin, the tensile strength decreases. Differential scanning calorimetry data showed that the sample without chitin has a glass transition temperature at –72 °C and a melting

point at 55 °C, while sample with 10 wt.% chitin showed a higher temperature inflection with an increase of about 9 °C (i.e., –63 °C) and a slightly higher melting point. The addition of chitin fillers has little effect on the glass transition. Thermogravimetric–differential thermal analysis indicated that the decomposition of chitin free sample starts at approximately 210 °C, while the decomposition of sample with 10 wt.% chitin begins at 290 °C. The inclusion of chitin improved the ionic conductivity, thermal stability, and mechanical properties of the electrolyte [82].

In the presence of fillers, the diffusion of the Li^+ ion is enhanced, since the fillers increase the free volume of the polymer chain. It should be noted that the mechanism of polymer crystallinity reduction does not depend on the chemical nature of the filler, but on the size, volume fraction, and shape of the filler [96]. The quantitative content of fillers to achieve optimal diffusion of the Li^+ ions will differ for different particle sizes. Inert fillers such as TiO_2, SiO_2 are often used in amounts as low as few percents to achieve optimum ionic conductivity. However, as the content of the inert filler increases, the mechanical strength of the polymer membrane decreases. On the contrary, active fillers such as LLZO, LAGP, etc. have high ionic conductivity and can participate in the transport of Li^+ ions, therefore, with an increase in the active filler content, the conductivity can increase accordingly. Therefore, depending on the properties and content of the active filler and polymer, the optimal content for achieving the maximum electrical conductivity is different [97]. The inclusion of a filler in the GPE can suppress the formation of lithium dendrites by improving the mechanical properties of the polymer matrix, as well as due to the formation of a uniform flow of Li^+ ions at the Li-metal/electrolyte interface [98].

4.3.3. Effect of lithium salt

The choice of salt for any electrolyte is primarily based on their physicochemical properties: solubility, degree of electrochemical dissociation, ionic mobility, transfer number. It is also important to consider thermal and electrochemical stability, toxicity, and cost.

Perfluoroalkyl sulfonic-type conductive salts, such as LiTF ($LiSO_3CF_3$), LiTFSI ($LiN(SO_2CF_3)_2$), LiBETI ($LiN(SO_2C_2F_5)_2$), have good solubility, high ionic conductivity, and electrochemical stability [73]. The larger the lithium salt anion, the higher the ionic conductivity is. Therefore, an anion with a well-delocalized negative charge and low basicity is preferable for high ionic conductivity and plays a dominant role in the reaction. The ion mobility increases with decreasing anion size in the series: $LiBF_4 > LiClO_4 > LiPF_6 > LiTf > LiTFSI$ [99]. But compared to $LiBF_4$, $LiClO_4$ has a strong oxidizing power,

making it unsafe to use in LIB. Despite the high ionic conductivity of $LiPF_6$, it easily decomposes in the presence of moisture and reacts with electrolytes at elevated temperatures forming HF. This salt can spontaneously decompose into LiF and PF_5. In addition, P–F bonds are very sensitive to traces of moisture in the electrolyte solvent. Therefore, HF is inevitably present in all $LiPF_6$ solutions, which causes the transition metal cations of the cathode materials to dissolve and leads to a decrease in capacity [100].

When the LiTFSI salt is added, the decomposition temperature of the electrolyte decreases and a weight loss above 150 °C is observed due to the decomposition of the LiTFSI. The higher thermal stability of this electrolyte allows operation of a lithium battery even at temperatures above 80 °C. The behavior of ions in electrolytes in terms of conductivity usually obeys Vogel–Fulcher–Tammann–Hesse equation, from which it can be concluded that the conductivity increases with increasing temperature. This indicates the absence of a physical transition or segregation phenomenon occurring within the temperature range under study [101].

Goncalves et al. reported on a solid polymer electrolyte based on a PVDF-HFP and LiTFSI copolymer and evaluated the effect of LiTFSI content on ionic conductivity [102]. This work showed that PVDF material as a solid electrolyte has a certain effect on the dissociation of lithium salt. However, a pure polymer with a lithium salt system has difficulties to meet the needs of ion transport. The performance of a battery made with such electrolytes is worse than with organic liquid electrolytes. Another problem is that polymers are much less thermally stable than inorganic materials and can ignite as well as decompose at high temperatures. The main strategy is to combine the polymer with other materials or add inorganic materials to the polymer base, so that the solid electrolyte has the advantages of both, with good mechanical properties and interfacial compatibility, while significantly improving ionic conductivity [74].

Salt concentrations directly affect the solvation of Li^+ ions in solution, as well as other electrolyte properties, including the formation of interfacial boundaries. In most non-aqueous electrolyte solutions, the maximum conductivity occurs at a salt concentration of about 1 M [103]. However, high electrolyte conductivity does not necessarily mean high Li^+ content.

4.3.4. Solid polymer electrolytes and ceramic electrolytes

The first solid polymer electrolyte (SPE) for lithium energy was proposed by Armand and Duclot in 1978 [75]. SPE is used for batteries that can operate in harsh environments due to a high modulus of elasticity, good thermal

and chemical stability, and a wide electrochemical window. The interest in SPE development is fueled by new high-performance materials, stringent safety regulations, and new applications [104]. Ionic conductivity in SPE is assumed to occur in the amorphous and crystalline phases: in the amorphous phase, the segmental motion of polymer chains promotes the migration and jumping of alkali metal ions from one coordination center to another; in the crystalline phase, conductivity occurs through ordered domains, polymer chains, and anions. In this regard, there is a special interest in amorphous polymer electrolytes, for example, polyester diacrylates [105].

To improve ionic conductivity and thermal stability, PMMA and SiO_2 aerogel were added to SPE based on PEO/EC/LiClO$_4$. SPE with PEO:PMMA ratio of 8:1 and 8 wt.% SiO_2 aerogel showed high electrical conductivity ($1.35 \cdot 10^{-4}$ S/cm at 30 °C) and good mechanical stability. Thus, SiO_2 aerogels with high specific surface area and mesoporosity can play an important role in the development of solid polymer electrolytes with an improved structure and stability [9].

Sulfide electrolytes belong to the class of electrolyte materials with the highest ionic conductivity ($3.96 \cdot 10^{-3}$ S/cm). Solid sulfide electrolyte $Li_{10}SnP_2S_{12}$ (LSPS) has attracted wide attention due to its low manufacturing cost and outstanding performance. However, its ionic conductivity and resistance to lithium and air needs to be improved. The introduction of oxygen into sulfide electrolytes can be a way to increase the ionic conductivity of sulfides as well as to improve electrochemical stability. The exposure of $Li_{10}Sn_{0.95}P_2S_{11.4}O_{0.5}$ (LS$_{0.95}$PSO$_{0.5}$) to air decreases ionic conductivity, which proves that doping with O improves the stability of the electrolyte in air. Given that the chemical bond between Sn and O is stronger than between Sn and S, oxygen substitution is expected to improve thermodynamic stability. Cells with electrolytes LSPS and LS$_{0.95}$PSO$_{0.5}$ were cycled. The increase in the number of cycles raises the polarization voltage of LSPS, which indicates a more complex interfacial reaction between LSPS and lithium metal. Therefore, LS$_{0.95}$PSO$_{0.5}$ has a better electrochemical lithium resistance than LSPS. The LS$_{0.95}$PSO$_{0.5}$ battery consumes less capacity during the first charge-discharge process, which indicates fewer side reactions at the electrode/electrolyte interface. Although the discharge capacity decreases with cycling, the introduction of oxygen into sulfide electrolytes may be a way to improve ionic conductivity and electrochemical stability [106].

In article [107] ceramic electrolyte $Li_2O–Al_2O_3–P_2O_5–B_2O_3–K_2O$ was synthesized, studied and optimized. Thermal treatment of samples is a necessary operation that should be carefully controlled in the synthesis of a solid electrolyte. During heat treatment, defects appear and affect the electrical conductivity of the material. According to measurements, heat treatment of samples at 900 °C provides the best values of electrical conductivity up to $4.28 \cdot 10^{-4}$ S/cm.

Currently, research on inorganic electrolytes is mainly focused on oxide materials, such as $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO). They have excellent thermal stability and safety. Their high modulus of elasticity helps suppress the growth of lithium dendrites. However, the high hardness and high modulus of elasticity also make it difficult for inorganic electrolytes to come into close contact with the electrode. Reducing the thickness of solid inorganic materials is considered an effective strategy to address these limitations [74].

In Ref. [108] it was proposed to use potassium lithiostannate $KLiSnO_2$ with a sufficiently high potassium ion conductivity, but the presence of easily reduced Sn^{4+} cations in the composition challenges its use as a solid electrolyte in high-temperature batteries (e.g., conductivity of 84% dense ceramics at 227 °C is 0.23 S/m). The problem was solved by replacing the Sn^{4+} cation with Zr^{4+}. The structural properties of the $K_2O–Li_2O–ZrO_2$ composite are very different from the layered potassium lithiostannanate. The absence of wide channels in it complicates cationic transport, but its ability to selectively absorb carbon dioxide promises further research [109].

Most of the electrolytes used in commercial batteries today are non-aqueous organic solutions. GPEs have many properties of interest for safer and environmentally friendly batteries. To improve the properties of such electrolytes and use them in commercial rechargeable batteries, further optimization of the composition should be carried out: electrolyte components, metal salts, solvents and additives.

Liquid electrolytes have high energy density, superb contact with electrode and excellent rate capability, but demonstrate low safety, poor electrochemical stability and the inevitable growth of dendrites. On the contrary, solid electrolytes have high safety, block the growth of dendrites, but have poor cyclicity, low ion conductivity and a weak electrode interface. GPEs combine the advantages of both solid and liquid electrolytes, they demonstrate excellent flexibility, processability, improve safety features, minimize the dendrite growth and enhance resistance to variation.

5. ALTERNATIVES TO LITHIUM IN ENERGY STORAGE DEVICES

The scale of lithium-based devices production may exhaust this material in future [110]. Lithium demand is forecast to increase by 11 times between 2020 and 2030 [111]. The key drivers are the expected transition to green and renewable energy, the ubiquity of portable electronic devices and the

Table 3. Characteristics of some metals used in batteries [112].

Characteristic	Metal			
	Li^+	Na^+	K^+	Mg^{2+}
Cation radius, Å	0.76	1.02	1.38	0.72
Prevalence in the Earth's crust, ppm by mass	20	23000	21000	23000
Theoretical specific capacity, mA·h/g	3862	1166	686	2205
Redox potential vs SHE in aqueous medium, V	−3.04	−2.71	−2.93	−2.37

growing popularity of electric vehicles. The main alternatives to lithium are sodium, potassium, and magnesium. The characteristics of these metals are presented in Table 3.

5.1. Sodium-ion batteries

In the 90s of the XX century as a cheap alternative to LIBs sodium-ion batteries were developed. Many years later in 2015, Faradion Ltd showcased their first product as an e-bike, powered by sodium-ion batteries with an energy greater than 400 W·h per pack. This battery had $Na_aNi_{1−x−y−z}Mn_xMg_yTi_zO_2$ layered oxides (130 mA·h/g) as the cathode and hard carbon anode (230 mA·h/g) [113]. A sodium-ion battery is almost identical to a LIB in terms of electrical characteristics, but it has a number of advantages over it:

1. The cost of the materials used in it is much lower, because sodium is about 100 times cheaper than lithium;

2. Sodium-ion batteries are safer as they are less likely to explode and ignite compared to LIBs;

3. In sodium-ion batteries, unlike LIBs, both aqueous and non-aqueous electrolytes can be used. The limited electrochemical stability window of water results in lower voltage and limited energy density sodium-ion batteries when using aqueous electrolytes;

4. The ability to store sodium-ion batteries at a charge level of 0%, while for lithium-ion batteries, the charge level must be at least 30% [114].

The main problems in the use of sodium-ion batteries are the high value of irreversible capacity, its decrease as a result of cycling, and low values of electronic and ionic conductivity [115]. The key point of the electrochemical process is the incorporation of ions into the electrode. The faster and easier it passes, the greater the instantaneous power can be. If the process is slow, the battery will not be able to provide the current needed to operate the device. This is precisely the difficulty in developing a sodium-ion battery. A conventional carbon electrode is not suitable because sodium ions due to their size, do not integrate well into the graphite structure.

In this regard, hard carbon (HC) has attracted particular attention as a promising anode material. Hard carbon is mostly known as non-graphitable carbon, it is composed of disordered turbostratic nanodomains and has no c-direction ordering. The exact structure, the size of the graphite microcrystalline zone, the number of carbon layers and nanopores depend on the carbonization temperature [116].

Stevens and Dahn [117] were the first to report the use of HC as an anode with a high reversible capacity of more than 300 mA·h/g. In recent years, the properties of HC anodes have improved rapidly. Nitrogen-doped HC with a soybean residue was described in Ref. [118], as well as nitrogen-doped amorphous carbon nanofibers obtained from chitin were used as anodes in Ref. [119]. Unfortunately, the practical use of solid carbon anodes is largely limited by their low initial Coulomb efficiency.

As cathodes for Na-ion battery, layered oxides, analogues of Prussian Blue (PBA), and polyanions are promising materials [113].

5.2. Potassium-ion batteries

Potassium is an attractive alternative to lithium as an anode. K^+ ions exhibit faster ionic diffusion in electrolytes due to weaker interaction with solvents and anions than that of Li^+ ions [120]. However, its use is complicated by the growth of dendrites and the increase in volume during cycling. Second, the low diffusivity of K^+ in the solid electrode materials constitutes limitations on the rate performances. Finally, the electrolyte in potassium-ion batteries suffers from severe decomposition and several parasitic reactions due to the low potential of K^+/K redox [121]. To circumvent these problems, Ref. [122] proposed the synthesis and application of nitrogen and zinc doped porous carbon nanofibers that act as a matrix for potassium metal. Experimental and theoretical measurements show that carbon nanofibers induce a uniform distribution of potassium and prevent the growth of dendrites during cycling. Carbon material with potassium was tested as a negative electrode in combination with a sulfur-based positive electrode and a non-aqueous electrolyte solution in a coin cell, the average voltage was 1.6 V, the capacity was about 470 mA·h/g after 600 cycles at room temperature. Numerous studies have focused on optimizing the potassium-containing composition analogues by doping them with Fe, Co, Ni, Zn and Mn ions. Huang et al. [121] synthesized a multivariate potassium-containing analogues with Ni, Co, and Fe by controlling the Co and Fe content through the synthesis conditions. This cathode could deliver a discharge capacity of up to 135 mA·h/g.

In Ref. [123] a full K-ion battery was constructed from commercial Bi as the anode, 1.0 M of KPF_6 in dimethoxyethane as electrolyte, and Prussian Blue $K_{0.72}Fe[Fe(CN)_6]$ as the cathode. The battery demonstrated a high capacity retention of 86.5% after 350 cycles and a high energy density of 108.1 W·h/kg at a power density of 566 W/kg.

5.3. Magnesium-ion batteries

Magnesium is also a promising material for a post-lithium battery: its melting point is higher, it retains a charge longer, and the energy density of such a battery can be five times higher than that of lithium-ion. Magnesium practically does not form dendrites, which allows the battery not to lose its properties over many cycles. A promising material for the cathode of a magnesium battery can be composite $MgCr_2O_4$ [124].

The disadvantage of magnesium batteries is a film similar to the one in LIBs, which is formed on the surface of the magnesium anode when cycling in organic solvents. The problem of film formation at the anode can be avoided by switching from magnesium to magnesium-ion batteries, based on the fact that magnesium ions are reversibly introduced into the anode and cathode materials [125]. Currently, work is underway to find the most suitable material for anodes of magnesium-ion batteries (MIB). Some materials, for example bismuth and tin, have shown good properties, such as low reduction potential and relatively high theoretical specific capacity, but yet they are far from being used in practical application systems due to their poor electrochemical stability during long-term cycling. Thus, dual-phase alloy anodes have been proposed as a possible solution, and in many cases, they have shown superior properties compared to both bismuth and tin alone, mainly due to the better kinetics and high reversibility that the dual phase provides [126]. Other problems hindering the development of MIBs include obtaining suitable chloride-free electrolyte solutions with wide electrochemical windows, in which magnesium can behave reversibly, and the development of new cathodes that are less sensitive to the composition of electrolyte solutions.

Because of low diffusion kinetics and strong polarizability of the electrode and, therefore, low performance of magnesium-ion batteries, research is being conducted in the field of hybrid materials. Ref. [111] reported on the development of a magnesium/lithium-ion battery with Mg^{2+} and Li^+ as charge carriers. However, such a battery has not reached the operating electrochemical characteristics yet.

6. SUMMARY

The wider use of LIBs is limited by issues of safety and cost of the materials used. The safety and performance of LIBs can be greatly improved by careful selection of electrode, separator, and electrolyte materials, and by optimizing battery design. Although LIBs have improved a lot since their invention in the early 1970s, even today's commercial LIBs do not meet all of current consumer needs.

For LIBs, new materials such as transition metal oxides have a high potential as an anode substance. Also,

some widely used electrode materials have been successfully modified by doping, coating, and combination with other materials. Modern electrolytes based on carbonate esters are widely used, but do not meet most of the requirements for advanced LIB. They have a narrow operating temperature range of −20 to +50 °C, a limited 4.3 V operating window, and are highly flammable. Composite GPEs, which combine the advantages of solid and classical liquid electrolytes, are promising. A wide range of possible fillers for GPE opens up a lot of scope for creativity. Thus, the advent of new electrode materials and electrolytes may have great potential to make LIBs more efficient.

Sodium- and potassium-ion batteries based on cheap sodium and potassium resources are likely to offer a significant cost advantage for stationary applications such as electrical grids. In addition to price, another driving force behind the development of post-lithium technologies is the need for higher energy density to meet the needs of electric vehicles, including electric cars, electric omnibus and electric aircraft. The use of GPE or SSE also improves battery safety by preventing electrolyte leakage or fire.

Mg-based batteries have the potential to provide a unique combination of high energy density and low cost as a post-lithium technology. However, MIBs that have been studied to date do not meet researchers and consumers' expectations as high energy density devices.

The fact that some of the problems are based on the same scientific principles and can be studied using similar LIB approaches may accelerate the development of post-lithium technologies. In summary, LIBs are still efficient and reliable energy storage systems and are widely used in portable electronics and electric vehicles.

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Обзор материалов для электродов и электролитов литиевых аккумуляторов

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Аннотация. Литий-ионные аккумуляторы по-прежнему являются эффективными и надежными системами хранения энергии и широко используются в портативной электронике и электромобилях. В данном обзоре описаны типы существующих в настоящее время литиевых аккумуляторов, системы с анодами, катодами и электролитами из различных материалов, а также методы их исследования. В частности, он начинается с краткого введения в принципы работы литий-ионных аккумуляторов и устройства ячеек, а затем дается обзор методов исследования аккумуляторов. Особое внимание уделено использованию наноразмерных частиц для модификации электродов и электролитов, а также сополимеризации индивидуальных полимеров гель-полимерного электролита. В обзоре анализируются возможные будущие разработки и перспективы пост-литиевых аккумуляторов.

Ключевые слова: литий-ионные аккумуляторы; гель-полимерные электролиты; твердотельные электролиты; электроды; наночастицы