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Primary chemical current sources in research studies of recent years: a review

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Abstract: The paper reviews the world research in the field of primary chemical current sources (CCS) from 2016 to the present. Publications in the field of development and modification of anode and cathode materials for primary CCS, as well as electrolytes used in them, are considered. Both studies on classical materials that have proven themselves in recent decades, and the developing direction of creating environmentally friendly and safe elements are noted. Increasingly, alloys are being used to improve the discharge characteristics of batteries. The use of carbon materials, including graphene and graphene oxide with their unique properties, is widespread. Polymer electrolytes have been developed as a profound way to create safer energy sources. The number of scientific works in the field of primary CCS indicates the continuing need for efficient non-rechargeable systems for both domestic and specialized needs of mankind.

Key words: primary battery, composite materials, polymer electrolyte, graphene, graphene oxide, lithium batteries, energy source

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1. INTRODUCTION

Modern life is impossible to imagine without portable energy sources. From watch on the wrist to launch of the spacecraft to the borders of the Solar System - everywhere there is a need for the generation of electrical energy. Just as torches once lit a path in darkness, progress opened up new opportunities for humanity, replacing these torches with lanterns. In the early 18th century,

in less than a century, the world changed forever. The appearance of the first chemical current sources (CCS) marked the beginning for an extensive field of research, in which work is constantly being carried out to improve existing systems and create new ones that meet rigid requirements of technical progress.

CCS is a device in which the energy of chemicals is converted into electrical energy [1-11]. CCS consists of one or more galvanic cells – two electrodes separated by an electrolyte. The execution of a chemical reaction is due to the

nature of these constituents. At the boundaries between the electrodes, first-class conductors, and the electrolyte, a second-class conductor, current-forming reactions occur – oxidation and reduction reactions. The electrode on which the oxidizing agents are oxidized is called the anode, and the electrode on which the oxidizing agents are reduced is called the cathode. At the negative anode, the reducing agent is oxidized, the resulting free electrons pass through the external circuit to the positive cathode, where they participate in the oxidant reduction reaction.

Table 1

Types and fields of application of batteries

Battery type	Application area	Devices
Saline (manganese-zinc)	At home	- remote controls, clocks, scales, simple children's toys, electronic thermometers and other devices with low power consumption
Alkaline (manganese-zinc)	At home	- scales, electronic clocks, remote controls, lamps
	Media	- cameras with flash, camcorders, lighting systems, radios, portable players
	Military	- radio beacons, radios, flashlights, radio-controlled models
	Kids toys	- radio-controlled models, toys with a speaker, etc.
	Medicine	- electronic devices for measuring of blood pressure, body temperature, hearing aids, Holter monitors
Silver (silver-zinc)	Office equipment	- PC motherboards, laser pointers, calculators
	Military	- microflashlights, microchips, radio beacons
	Medicine	- hearing aids, pacemakers
	Other	- musical cards, watches
Mercury	Medicine	- pacemakers, hearing aids
	Military	- night vision devices, portable radio equipment for military purposes, spacecraft, alarm devices, rescue equipment, combat missiles and torpedoes
	Other	- electronic clocks, photoexposure meters, cameras, monitoring systems, control devices for drilling oil and gas wells, rescue equipment
Lithium	IT	- sensors for intelligent parking systems, environmental monitoring equipment, data loggers, energy management systems, equipment for "smart buildings"
	Medicine	- Defibrillators, respirators and oxygen concentrators, continuous monitoring equipment, mobile diagnostic equipment, infusion pumps, telemedicine equipment, pacemakers
	Military	- portable radio communications, night vision devices and thermal vision devices, shooting accuracy training simulators, gas detectors, field radars, weapon systems and ignition systems, flashlights and lamps
	Oil and gas	- systems for measuring parameters while drilling, LWD devices, equipment for pumping and operating wells, subsea equipment, devices for working in an explosive environment, equipment for seismic exploration, pipeline cleaning devices
	Professional electronics	- professional handheld devices and portable devices, professional monitors, ticket terminals and information desks, transport integrated information facilities
	Safety	- security surveillance systems for home and swimming pool, smoke and CO ₂ detectors, security systems with blocking, video surveillance, wireless sirens, manual fire alarms, passive infrared presence detectors, glass break detectors, perimeter protection, biometric readers, non-contact card readers and complex wireless alarm systems
	Tracking	- equipment tracking systems, vehicle tracking systems, toll road transponders
	Energy metering and control	- automatic metering devices, intelligent metering systems for electricity, water, gas and heat, stationary telecommunication devices for the global computer network
	Other	- buoys, signal lamps, beacons, life jackets, toys (musical, radio-controlled), scales, watches, laptops, microchips, etc.

Thus, a stream of negatively charged electrons creates a current.

There are several types of CCS. Primary CCS are called batteries, current sources intended for single use. Rechargeable batteries are secondary CCS, they are capable of being repeatedly charged and discharged by converting the chemical energy of active substances into electrical energy and backward. There are current sources, the active substances (fuel and oxidizer) of which are outside the cell and are supplied separately – fuel cells.

Nowadays, rechargeable batteries are the most popular. Due to the reversibility of chemical reactions inside the storage battery, such a power source can be reused many times. Rechargeable batteries are found in cars and mobile phones, and are used in household appliances and electronics. Thanks to the rechargeable batteries, the carriages are illuminated and computers work in case of an emergency power outage. It seems that rechargeable CCSs should already oust its simplest competitors from the market.

However, the primary CCSs, batteries, are still needed where the use of rechargeable batteries is difficult or economically impractical. Often, without batteries, the work of a child's toy, a medical device, and even a spacecraft is impossible (**Table 1**).

There is a wide variety of primary CCSs on the market today. Some of systems are presented in **Table 2** [1].

Despite the apparent simplicity of the design, the number of proposed modifications to the shape and composition of the battery is growing steadily every year. Along with traditional materials – lithium, various alkali metals, lead and manganese compounds – multicomponent alloys, rare metals, organic compounds and even air are used to create anodes and cathodes. Separators are made of paper, plastic, modified fibers. The composition of electrolytes ranges from complex biocompatible compounds to plain water, and liquids are replaced by gels and solids. And if the inner part of the batteries remains more the subject of interest of

Table 2

Current-producing reactions and theoretical parameters of the main primary CCS

System	Current-generating reaction	Ucc, B	Theoretical energy density, W·h/kg
Zn NH ₄ Cl MnO ₂	2MnO ₂ + Zn + 2NH ₄ Cl = 2MnOOH + [Zn(NH ₃) ₂]Cl ₂	1.7	260
Zn ZnCl ₂ MnO ₂	2MnO ₂ + Zn + 2H ₂ O + ZnCl ₂ = 2MnOOH + 2Zn(OH)Cl	1.6	208
Zn KOH MnO ₂	2MnO ₂ + Zn + 2H ₂ O = 2MnOOH + Zn(OH) ₂	1.6	312
Zn KOH HgO	HgO + Zn = Hg + ZnO	1.35	256
Zn KOH Ag ₂ O	Ag ₂ O + Zn = 2Ag + ZnO	1.6	288
Zn KOH Воздух	O ₂ + 2Zn = 2ZnO	1.64	1344
Zn NaOH CuO	CuO + Zn + 2NaOH + 2H ₂ O = Cu + Na ₂ [Zn(OH) ₄]	1.06	215
Cd KOH HgO	HgO + Cd + H ₂ O = Hg + Cd(OH) ₂	0.91	140.6
Mg Mg(ClO ₄) ₂ MnO ₂	2MnO ₂ + Mg + 2H ₂ O = 2MnOOH + Mg(OH) ₂	2.96	675
Li LiClO ₄ , ПК MnO ₂	MnO ₂ + Li = LiMnO ₂	3.5	1075
Li LiBF ₄ , ПК (CF) _n	(CF) _n + nLi = nLiF + C _n	2.82	2192
Li LiClO ₄ , ДОЛ CuO	CuO + 2Li = Cu + Li ₂ O	2.24	1285
Li LiClO ₄ , ДОЛ Cu ₄ O(PO ₄) ₂	Cu ₄ O(PO ₄) ₂ + 8Li = 4Cu + Li ₂ O + 2Li ₃ PO ₄	2.8	1146
Li LiClO ₄ , ПК, ДМО FeS ₂	FeS ₂ + 4Li = Li ₂ S + Fe	1.75	1273
Li LiBr, АН SO ₂	2SO ₂ + 2Li = Li ₂ S ₂ O ₄	3.1	1175
Li LiAlCl ₄ , SOCl ₂ SOCl ₂	SO ₂ Cl ₂ + 4Li = S + SO ₂ + 4LiCl	3.66	1477
Li LiAlCl ₄ , SO ₂ Cl ₂ SOCl ₂	SO ₂ Cl ₂ + 2Li = 2LiCl + SO ₂	2.91	1405
Li LiAsF ₆ , ПК, ДМЭ Ag ₂ CrO ₄	Ag ₂ CrO ₄ + Li = Li ₂ CrO ₄ + 2Ag	3.35	515
Li LiI ₂ I ₂ , ПВП*	I ₂ + 2Li = 2LiI	2.8	560

*polyvinylpyridine

specialists, then the variety of shapes and sizes of batteries is now known to absolutely anyone. Cylindrical, rectangular, round cases have long found their standard size names like AA, AAA, C, D, etc. New types of batteries regularly add to this list, and what was a prototype in the laboratory yesterday is now becoming the new standard for power supplies.

This review aims to analyze the work in the development of primary CCS over the past 7 years. The main attention is paid to the synthesis and research of cathode and anode materials, as well as electrolytes.

2. ANODE

The structural element of the primary current source, which determines the type of battery, is the anode. Currently, anode materials based on zinc, nickel, magnesium, aluminum, lithium, as well as their alloys, that is, multicomponent systems, are widely used [12].

2.1. MULTI-COMPONENT MATERIALS

To obtain an anode material based on a multicomponent system, the casting method is used in most cases. Mixture of metal powders is melted in a furnace in a gas environment and poured into a prepared form, and at the next step the workpieces are subjected to homogenizing annealing. Using this technique, anodes for Mg-Air batteries are made based on AZ 31, Mg - Li - Al - Ce, Mg - Al - Pb alloys, which have an energy density of about 25 mW/cm². In order to improve this indicator, an alloy based on Mg - Al - Sn was obtained [13]. The discharge characteristics shown that Mg-Air cell on the basis of alloy Mg - Al - Sn provides a higher peak energy density - 94.1 mW/cm² - than that of the alloy anodes AZ 31, Mg - Li - Al - Ce, Mg - Al - Pb. In addition, the resulting alloy was found to have a lower content of harmful discharge products.

Extruded Mg-9Al-xIn alloys are systematically studied as a potential anode material for primary Mg-air batteries [14]. Research has shown that the addition of indium to a magnesium alloy

has a strong positive effect on many parameters. Efficiency of the anode based on Mg-9Al-0.5In is 78.2% at a current of 150 mA/cm², which is significantly higher than the values of magnesium alloys without indium. In addition, the test alloy exhibits a high cell voltage and energy density of about 76.8 mW/cm².

A significant effect on the structure and, respectively, the energy parameters of the final battery has alloys annealing temperature [15]. This is illustrated by the example alloy and Mg-6%Al-1%Sn-1%In (wt.%). Sheet blanks with a thickness of 2 mm were obtained by hot extrusion. After annealing at the temperature of 200°C, 250°C and 300°C, the alloy sheets were tested. As shown by the test results, cells with an anode of Mg-Al-Sn-In have the best performance and can provide an average voltage of 1.527 V at a specific energy of 98.3 W·h/kg. Such results are substantiated by a homogeneous microstructure, fine grains, and small crystal defects.

Binary alloys Mg-xLa (x = 0.2-0.8 wt.%) were investigated as anode materials for magnesium-based batteries. The results show that the magnesium matrix corrosion rate decreases with lanthanum alloying, and it can be associated with the formation of a protective film on the surface of the alloy, containing La₂O₃. However, with an increase in the content of lanthanum, the protective properties deteriorate: an increase in the microgalvanic corrosion reaction is observed, caused by an increase in the amount of the intermetallic phase Mg₁₂La; however, all Mg-La alloys had a corrosion rate less than pure magnesium. Mg-La alloys with a low content of lanthanum (less than 0.6 wt.%) are attractive candidates for high performance anode material for magnesium-based batteries [16].

For the manufacture of anodes, not only the casting method is used, but also printing methods with the integration of laser technologies [17]. So, an anode was made of ink with aluminum nanoparticles (30-40 nm) using squeeze printing. In addition, a laser sintering method was used to

remove the organic solvent from the suspension and increase the conductivity of the printed anode. A Pt/C mixture was chosen as the active material of the cathode electrode, and a KOH based gel electrolyte was also used. This experimental cell at an operating voltage of 0.95 V provided a capacity of 239 mA·h/g and an energy density of 227 mW·h/g.

Now, due to environmental problems in general and the disposal of used batteries in particular, more and more biodegradable materials appear [18]. For example, AZ31 magnesium alloy containing 3% Al and 1% Zn was used as a replacement for pure magnesium, increasing the device life by more than six times, which significantly improved the maximum capacity and energy consumption of the battery, which was 5.2 mA·h and 67 mW respectively, although the area of the anode was a total of 0.8 cm².

2.2. MODERNIZATION OF STRUCTURE AND SURFACE

Anode surface treatment is also one of the promising directions for achieving high discharge characteristics of primary current sources [19]. In one of the studies, carbon materials were applied to the surface of aluminum anodes in order to improve the discharge characteristics of an Al-air battery. NaCl (2M) was used as electrolyte. In the course of research, it was revealed that carbon materials actually increase the values of discharge characteristics. The anodes were made of Al₁₀₈₅ and Al₇₄₇₅ alloys, which demonstrated specific capacities of about 700 mA·h/g and 1200 mA·h/g (at currents of 5 mA/cm² and 10 mA/cm²), respectively. A battery of 4 series-connected cells at a current of 5 mA/cm² had an operating time of 18 hours from a voltage plateau of 2V. This is explained by the fact that a gel consisting of aluminum hydroxide is formed on the surface of untreated aluminum anodes during the discharge process, which and prevents diffusion of hydroxyl ions. Carbon materials help to partially prevent the formation of this jelly-like texture.

The reverse situation is also possible – the improvement of carbon anodes with the help of metal alloys. A method for manufacturing flexible graphene batteries containing Ni₅₀Mn₃₅In₁₅ (NiMnIn), Ni₅₀Mn₃₀Ga₂₀ (NiMnGa), and Ni₅₀Mn₄₀Sn₁₀ (NiMnSn) magnetic alloy microparticles is presented. Anodes with magnetic alloy microparticles were treated with phosphoric acid, which leads to the formation of oxides of several metals on the surface of the alloys, which serve as charge accumulation sites. In addition, phosphoric acid has been used instead of lithium salts as an ion source, which allows more defects to form on graphene electrodes, increasing battery capacity. The maximum energy density (343.5 W·h/kg) and capacity (618.4 mA·h/g) were obtained for a battery containing NiMnGa microparticles with the highest porosity. The device voltage was 1.5 V, which is the same as the voltage provided by commercial alkaline primary batteries [20].

Despite the huge number of known galvanic systems and a certain set of metals used, work is constantly being carried out to improve the anode materials. So, batteries based on alkali metals require increased safety during the operation of the system, and for multicomponent systems, due to the diversity of its composition, the issue of effective disposal is relevant.

3. CATHODE

The cathode is the electrode on which the reduction reactions take place - the process of attaching electrons to the atoms of a substance, while its oxidation state decreases. This process is called oxidant reduction. The number of oxidants used in CCS is very large and continues to grow. However, in traditional power supplies with aqueous electrolyte solutions, relatively small amounts of oxidants are used. These are primarily oxides and hydroxides of metals: manganese, lead, nickel, copper, silver, mercury, copper, lead and silver chlorides, as well as atmospheric oxygen. With the advent of CCS with non-aqueous, molten and solid

electrolytes, as well as CCS with new aqueous solutions of electrolytes, the range of oxidants used has significantly expanded. Nowadays, oxides of cobalt, vanadium, chromium, sulfur, thionylchloride, sulfurylchloride, nickel and iron chlorides, iron and copper sulfides, fluorocarbon, bromine, iodine and other oxidizing agents have found application to one degree or another [1].

Work on the study of oxidants continues, and new active substances for cathodes are constantly appearing. In studies devoted to this topic, attention is paid not only to the synthesis of new cathode materials, but also to the mechanism of their destruction and analysis of the characteristics of batteries when using various cathode additives.

3.1. FLUOROCARBON

A number of works are devoted to fluorocarbons CF_x . The advantage of this material is that CF_x batteries are characterized by high energy and specific energy density, as well as a low self-discharge rate and a wide operating temperature range. Currently, research in this direction is mainly associated with various modifications of CF_x .

3.1.1. CF_x IN LITHIUM SYSTEMS

In the case of highly promising lithium systems, it is possible to improve the performance of the Li/CF_x system with the addition of polyaniline [21]. A uniform layer of polyaniline with a thickness of about 160-180 nm, deposited on the surface of the fluorocarbon, leads to an increase in the discharge current of the system. The conductive polyaniline coating provides external bonding between particles, facilitating conduction, resulting in high performance, discharge capacity, discharge voltage and energy density.

To increase the specific energy content of the Li/CF_x system, the CF_x -C cathode material was tested, obtained by adding isophorone diisocyanate, alkylphenolpolyethyleneglycol ester, and polyvinyl alcohol to CF_x , followed by high-speed dispersion, filtration, and

drying [22]. This material has improved electronic conductivity and greater porosity than conventional CF_x .

A strategy for developing a high-performance CF_x cathode using a metal-carbon oxide composite obtained from MOF (metal-organic frameworks) as a starting material is demonstrated. Such samples not only retain the MOF morphology, but also contain a large number of nanopores created during the fluorination process. Due to the advantages of the nanoporous structure, the samples fluorinated at various temperatures show the highest energy density of 2110.7 W·h/kg at a current density of 10 mA/g and the maximum power density of 6540 W/kg at 3000 mA/g. In addition, MOF-based fluorocarbon cathodes have the function of preventing swelling (volumetric expansion is not more than 12%). Moreover, the abundance of structures and low cost of MOFs suggest that it is a promising material for further improvement and popularization of primary Li/CF_x batteries [23].

It is known that the inclusion of a fluorocarbon in the cathode material of a CCS can contribute to a decrease in the self-discharge rate. For example, in primary batteries Li/MnO_2 . The addition of $(CF_x)_n$ to MnO_2 results in improved capacitance and voltage performance [24]. After storage for 60 days at 25°C, the specific capacity of a battery with a cathode made of MnO_2 decreases from 293 mA·h/g to 283 mA·h/g, and the specific capacity when using cathode material $MnO_2-(CF_x)_n$, on the contrary, increases from 312 mA·h/g to 326 mA·h/g. After storage for 30 days at 45°C, the self-discharge rate of batteries with MnO_2 and $MnO_2-(CF_x)_n$ is 9.21% and 1.92%, respectively.

The growth kinetics and orientation of LiF crystals, as the main discharge product of Li/CF_x batteries, are also studied using kinetic models in order to adjust the pore structure of the discharge product layer [25]. These studies may pave the way for the development of a new

electrolyte in the future for high energy density Li/CF_x systems.

3.1.2. CF_x IN NON-LITHIUM SYSTEMS

Typically, fluorocarbons are used in lithium systems. However, their use is also possible in other types of primary CCS. Thus, CF_{0.8} was first demonstrated as a cathode material for magnesium batteries with a high discharge capacity of more than 800 mA·h/g [26]. When using the APC (all-phenyl complex) electrolyte, the cell demonstrates a discharge voltage of 1.23 V and a high discharge capacity – from 813.4 mA·h/g at a discharge to 0.5 V. When LiCl salt is added to the electrolyte, the operating the Mg/CF_{0.8} voltage increases from 1.23 V to 1.6 V.

CF_x can also be used in a sodium anode system. Primary batteries of a new type Na/CF_x have been developed [27]. They are promising for low power applications. For batteries of this type, we studied the effect on the cathode material of carbon nanotubes (CNTs), which were conventional fluorinated CNTs (FCNT-x) and fluorinated graphitized CNTs (FGCNT-x). FGCNT-0.81 material demonstrated very high specific capacities – 798.8 and 751 mA·h/g in lithium and sodium batteries. Besides, the addition of fluorinated graphitized CNTs made it possible to achieve an energy capacity of 2006.6 W/kg in the Li/CF_x system and 1733.4 W/kg in the Na/CF_x system.

3.2. COMPOSITE MATERIALS

A composite material or composite is a multicomponent material made of two or more components with significantly different physical and/or chemical properties, which, in combination, lead to the emergence of a new material with characteristics that differ from the characteristics of the individual components and are not a simple superposition of them. At the same time, individual components remain unchanged in the structure of the composite, distinguishing it from mixtures and solid solutions. It is customary to separate the matrix and filler in the composition of the composite. By varying the composition of the matrix and

filler, their ratio, orientation of the filler, a wide range of materials with the required set of properties is obtained.

The synthesis of composite cathode materials is one of the most commonly used methods for improving the properties of batteries, and for this purpose, the aforementioned fluorocarbons are also used.

3.2.1. LITHIUM SYSTEMS WITH COMPOSITE MATERIALS

Systems with a lithium anode and the use of fluorocarbons as the cathode are of great interest. In order to improve the electronic conductivity of fluorocarbon in the Li/CF_x system, a polythiophene/fluorocarbon (PTh/CF_x (22.94% PTh)) cathode material obtained by insitu polymerization was studied [28]. This material provides 4997 W/kg power density at 4C current, while the maximum power density of a simple CF_x is only 1252 W/kg. A new composite material CF_x-MnO₂ has also been developed [29]. MnO₂ nanowires are synthesized by the hydrothermal method (a method that allows chemical synthesis to be carried out in autoclaves at high temperatures and elevated pressure) on the CF_x surface by insitu polymerization. They intertwine with each other and tightly cover the CF_x surface, forming a three-dimensional conductive framework and improving surface wettability, as well as increasing the capacitance and discharge voltage of Li/CF_x systems.

Also proposed is a solution to the problem of voltage drop at the beginning of the discharge of lithium batteries. Oxygen-containing CF_x was obtained by electrochemical oxidation of graphite in aqueous solution (47%) of hydrofluoric acid at high current densities (200 mA/cm²) [30]. The interlayer distance of such a material was 0.55 nm. The potential profile during the reaction and the X-ray diffraction pattern showed that in the resulting sample, both oxygen and fluorine are bound to each carbon layer. In addition, NMR analysis showed that the oxygen functional groups are uniformly distributed in the obtained samples. The capacity of such material reaches

550 mA·h/g, and the discharge voltage gradually decreases smoothly from an initial mark of 3.4 V.

By creating composites, it is possible to improve sulfur-based cathode materials [31]. Cu_xS was synergistically incorporated into a sulfur cathode in order to improve the specific discharge capacity. A battery with a developed cathode material with a properly selected ratio of sulfur and Cu_xS (40:60) demonstrates a plateau with a long discharge at 2.1 V, improved capacity and energy consumption.

3.3. GRAPHENE

Graphene is increasingly being used to improve the properties of cathode materials. Graphene is a two-dimensional allotropic modification of carbon, formed by a layer of carbon atoms one atom thick. This material has earned special attention to itself for its many useful properties. It conducts heat and electricity perfectly, and is ultra-lightweight and durable at the same time. In addition, graphene is biodegradable and does not pose a threat to the environment [32-47].

3.3.1. GRAPHENE IN LITHIUM SYSTEMS

To increase the energy density and specific energy consumption of Li/CF_x systems, a new hybrid cathode made of fluorine-containing graphene (FG) was proposed [48]. For comparison, two types of FG/S hybrid materials were prepared. In a hybrid cathode of the first type (FG/S-1), a mixture of FG and sublimed sulfur is prepared mechanically using a vortex generator. For the second type (FG/S-2), the melt diffusion method was used, the inclusion of sublimated sulfur in the FG occurred at 155°C for 12 hours in a vessel with argon. For both samples, the sulfur content was 30% of the total mass. Electrochemical tests have shown that hybrid cathodes lead to improved discharge characteristics, including increased specific capacitance and higher discharge voltage. The FG/S-2 cathode has a maximum energy density of 2341 W·h/kg and a maximum specific energy of 13621 W/kg.

The Lithium Thionyl Chloride battery is a promising primary battery due to its highest

theoretical operating voltage (3.6 V), excellent specific energy (up to 590 W/kg) and long operating temperature range [49]. However, disadvantages such as insoluble reaction product (LiCl) and incompletely dissolved sulfur deposited on the electrode can lead to battery failure. Spherical acetylene black is commonly used as the cathode material in this system. Due to its relatively low thermal and electrical conductivity, carbon black char cannot meet performance and safety requirements. The cathode material obtained by assembling acetylene black nanoparticles on graphene nanosheets is intended to improve the discharge characteristics of the system. Acetylene black char nanoparticles are distributed on graphene nanosheets in high concentration and form a micelle-like suprastructure. On the one hand, graphene nanosheets provide excellent mechanical characteristics and high electrical conductivity, as well as prevent the aggregation of acetylene black nanoparticles. On the other hand, the presence of acetylene black char can effectively insulate the graphene nanosheets from refolding and reduce the number of graphene nanosheets. The resulting hybrid of acetylene black char and graphene exhibits excellent discharge characteristics, providing a capacity of up to 1706 mA·h/g at a current density of 5 mA/cm².

3.3.2. GRAPHENE IN NON-LITHIUM SYSTEMS

The use of graphene is also possible in systems with metals other than lithium. Testing of cathode materials Mg/graphite and Mg/graphene was carried out [50]. The cathode material is prepared as follows: take 1 g of MgCl_2 and graphite (graphene), add 200 ml of ethanol to each and stir for 1 hour. Then the MgCl_2 / ethanol and graphite (graphene)/ethanol solutions are stirred for 2 hours. The solution is filtered and dried at 100°C. For comparison of properties, Mg/graphite, Mg/graphene, and a commercial cathode were taken. The conductivity of Mg/graphene (1080 $\mu\text{S}/\text{cm}$) turned out to be noticeably higher than that of Mg/graphite (90

$\mu\text{S}/\text{cm}$) and a commercial cathode ($10 \mu\text{S}/\text{cm}$). All research data show that Mg/graphene can potentially be used as a cathode in magnesium primary CCS.

It is shown that individual graphene monolayers with electrodeposited metals can be used as electrodes for built-in batteries [51]. The anode and cathode were realized by electrodeposition of zinc and copper onto graphene monolayers grown by chemical vapor deposition on a silicon substrate. Cells assembled from the obtained plates achieve capacities up to $15 \mu\text{A}\cdot\text{h}$ at a potential of about 1.1 V and a service life of up to 8 hours. Due to the economical design and simplicity of the presented circuit, such cells can become attractive for use in disposable on-demand power supplies for laboratory research or autonomous sensors.

3.4. ME-AIR

A number of works are devoted to the development and modernization of Me-air batteries. In the Me-air battery, the cathode consists of air and the anode is made of metal. The use of air makes these batteries fundamentally lighter and cheaper, so a lot of research is being done in this direction.

To develop a durable Me-air battery, MnO_2 cathode material was grown on nickel foam using a hydrothermal method [52]. Such unique conditions are used to obtain single crystals and particles of substances that are unstable near the melting point or, under normal conditions, are insoluble in water and other solvents. The foam provides optimum performance due to the balance of hydrophilicity and hydrophobicity. The electrodes synthesized by this method were tested in a primary Zn-air battery. The maximum specific energy density of $95.7 \text{ mW}/\text{cm}^2$ was reached at a discharge voltage of 0.8 V and a current density of $100 \text{ mA}/\text{cm}^2$. A stable discharge is completed in more than 14400 s at a current density of $20 \text{ mA}/\text{cm}^2$. The simplicity of preparation, as well as the high activity and stability of this

new air cathode has great potential for use in Me-air batteries.

As a powder cathode in another promising Me-air battery, MnO_2 was deposited onto a platinum substrate by electrodeposition [53]. At a current density of $330 \text{ mA}/\text{g}$, the cells reach a discharge capacity of $1000 \text{ mA}\cdot\text{h}/\text{g}$ with a specific energy consumption of up to $1890 \text{ mW}\cdot\text{h}/\text{g}$. These results show that the assembled Mn/ MnO_2 battery can occupy an important place in the field of energy storage, its performance is better than that of the classical Zn/ MnO_2 cell.

Also, Me-air batteries use silver electrodes deposited on CFP (Carbon Fiber Paper) to accelerate the oxygen reduction reaction [54]. The synthesis process is shown in the figure (Fig. 1). A battery assembled from Ag/CFP exhibits a discharge current density of more than $100 \text{ mA}/\text{cm}^2$ with an excellent specific energy density of $109.5 \text{ mW}/\text{cm}^2$, a high specific capacity of $2783.5 \text{ mA}\cdot\text{h}/\text{g}$ and a specific energy density of $4342.3 \text{ W}\cdot\text{h}/\text{kg}$.

Air batteries are usually made of hard and heavy materials such as metal or plastic, while a voluminous electrolyte solution in static or circulating mode is required to ensure their stable operation. Thus, they are less suitable for powering flexible and portable devices with lower power consumption. To solve this problem, a flexible and lightweight Al-air battery with low electrolyte content, which is made entirely on cellulose paper, has been developed [55]. The aluminum foil anode is embedded in the paper substrate during the papermaking process, while the breathable cathode is deposited on the

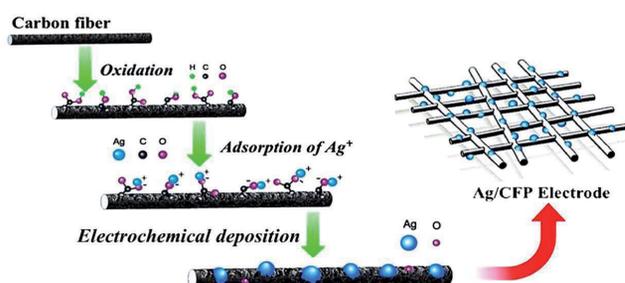


Fig. 1. Ag/CFP electrode fabrication.

surface of the paper using oxygen reduction ink. Despite its simple structure and low cost, this Al-air battery can provide a satisfactory specific energy density of 19 mW/cm², and its service life is 58 hours. The corresponding specific capacity is 2338 mA·h/g. In addition, the battery exhibits excellent flexibility.

3.5. ECO-FRIENDLY CATHODE MATERIALS

Increasingly, the works are investigating the possibility of making batteries from materials that are safe for the environment. The Fe/2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Fe-DDQ) primary CCS operated in pure methanesulfonic acid (MSA) was investigated [56]. Because it uses a large amount of iron and renewable materials such as DDQ and MSA, it is expected to be a cost-effective, single-use power system. Stainless steel (SS-304) is used as the iron source (anode) and the DDQ in MSA is used as the cathode. The Fe-DDQ battery is environmentally friendly, inexpensive and renewable. The operating voltage of the cell is 1.1 V, the maximum current density is 2 mA/cm², and the specific energy density is ~ 1.2 mW/cm².

A new chemistry is reported for an organic lithium primary battery that works by synergistically reducing 9,10-anthraquinone (AQ) and fluoroethylene carbonate (FEC) [57]. In the presence of FEC, the balance between the carbonyl and enol structures is disturbed and replaced by an irreversible process with the formation of methylene and inorganic salts (such as LiF, Li₂CO₃) as products. This irreversible AQ chemistry produces a high energy density of 1300 W·h/kg with a stable discharge voltage of 2.4 V, a wide operating temperature range (-40 to 40°C) and a low self-discharge rate. Combined with the advantages of low toxicity, simplicity and variety of synthesis methods, and readily available AQ, the chemistry of lithium organic batteries promises to be a new candidate for applications requiring low cost, high environmental friendliness and energy density.

Analysis of works focused on studies of cathode materials in primary CCS suggests that in this direction mainly work is being done on the synthesis of new cathode materials, and the most popular of them are graphite-containing materials. Also, great attention is paid to environmental friendliness, in particular, replacing lithium with safer metals. It should be noted that in spite of this, the highest discharge voltages and capacitance indices are achieved precisely on primary lithium CCS. They are trying to compete with Me-air systems; in such systems, high capacitance values are observed, but still low discharge voltages.

4. ELECTROLYTE

Electrolytes are substances that conduct electric current due to dissociation into ions in melts or solutions. These can be acids and bases, salts, some crystalline bodies (silver iodide, zirconium dioxide, etc.). All electrolytes can be divided into aqueous and non-aqueous; solid-phase electrolytes are isolated separately, the conductivity of which is justified by the movement of ions in crystal lattices.

4.1. IONIC LIQUIDS

Ionic liquids are examples of non-aqueous electrolytes. Ionic liquids – low-temperature molten salts with bulky cations and anions - are widely used as polar solvents and catalysts. Since they consist of "free" charge carriers, their use is especially in demand in the development of CCS. Ionic liquids have electrochemical stability, relatively high electrical conductivity and virtually no saturated vapor pressure.

Currently, work is being actively carried out in the direction of modernizing the chemical composition of electrolytes based on ionic liquids to improve the discharge characteristics of primary CCS. Using the example of an Al-air system with 1-ethyl-3-methylimidazolium oligofluorohydrogenate, the advantages of which are ultra-high conductivity, low viscosity and chemical stability in contact with oxygen and water, it was shown as an electrolyte that

practical results differ markedly from theoretical calculations [58]. In theory, such cells should have a capacity of about 227 mA·h, which is equivalent to 200 mAh/cm²; in practice, it was possible to obtain 70% of the theoretical calculations – up to 160 mA·h, which is equivalent to 140 mA·h/cm². Analysis of the battery components after complete discharge of the cell showed the presence of Al₂O₃ on the air cathode and active dissolution on the surface of the aluminum anode. To solve this problem, it was proposed to use ionic liquid electrolytes with tetrabutylammonium dihydrofluoride (TBAH₂F₃) in the Al-air system [59]. Due to the formation of a protective layer of Al_xO_yF_z on the aluminum surface, the formation of an oxide film is prevented and thus higher discharge values are ensured due to the more active surface.

4.2. POLYMER ELECTROLYTES

There is now a worldwide need to develop sustainable, safe and clean energy resources. One of the key directions for the implementation of this requirement is the development of new solid polymer electrolytes, which allow avoiding the leakage and release of toxic compounds during the operation of CCS. Systems based on biodegradable electrolytes are used in the medical field for electrical stimulation of tissue regeneration, in the environmental field to minimize environmental pollution.

Solid electrolytes are thin conductive membranes with a thickness of about 100-200 microns, obtained by mixing solutions of salts or acids and their subsequent drying [60-62]. The choice of the optimal composition of electrolytes is carried out after studying the energy characteristics of membranes obtained from solutions with different concentrations of precursors.

Due to the presence of high ionic reducibility, good biocompatibility, and a wide window of electrochemical potential, a promising material is a polymer electrolyte based on silk fibroin with choline nitrate (SF-[Ch][NO₃]) [63]. In

an experimental cell, such an electrolyte is a conductive membrane that allows the battery to operate for 45 days from a voltage plateau of about 1.03 V.

Polysaccharides are widely used biopolymers with properties suitable for the manufacture of high-performance polymer electrolytes. In particular, algae-based polysaccharides are promising environmentally friendly and biodegradable alternatives to conventional polyelectrolytes. Algae-based polysaccharides meet the key requirements for high performance polymer electrolytes – dominant amorphous phase, solubility, and the ability to form cross-linked networks with additives that improve ionic conductivity. Many of the optimized polymer electrolytes far exceeded the minimum ionic conductivity of electrolytes of 1 mS/cm. In addition, the mechanical properties of the algae-based hydrogel allow the creation of fully personalized wearable and biocompatible devices [64].

4.3. WATER ELECTROLYTES

Water electrolytes, that is, aqueous solutions of salts capable of dissociation into ions, are used quite widely in the creation of CCS. Despite the great popularity of non-aqueous electrolytes and the growing interest in polymer electrolytes, work in the field of aqueous electrolytes is still ongoing.

Changes in the energy parameters of systems with aqueous electrolytes can be achieved by introducing complexing elements [65]. The effect of adding two strong complexing agents at different concentrations to the aqueous electrolyte of a Mg-air battery was investigated. At the first stage, several organic complexing agents with different ability to form complexes Fe³⁺ and Mg²⁺ were investigated in order to assess their influence on the discharge behavior of the anode (pure magnesium). In the course of this study, nitrilotriacetic acid and tyrosine were chosen as complexing agents. The results obtained during the discharge of the cells indicate that the addition of tyrosine and

nitrilotriacetic acid to the electrolyte of a water-based Mg-air battery improves the discharge potential of the battery at concentrations in the ranges of 0.1-0.001 M and 0.1-0.01 M. The maximum improvement in potential during a discharge for 24 h, obtained in these two cases, was about 210 mV and 200 mV, respectively. The results allow us to conclude that strong complexing agents in the composition of an aqueous electrolyte are able to effectively activate the anode and provide a higher discharge potential.

The electrolyte plays an important role in primary CCS, often determining the shape of the entire battery. The realization of the potential of the cathode and anode materials depends on his choice, which is confirmed by continuous research in this area. Striving for environmental friendliness, safety in use and high compatibility with a wide variety of devices, solid materials and biological media are increasingly used as electrolytes.

5. CONCLUSION

Chemical power sources have firmly established their position in modern life. At first glance, the appearance of accumulators and fuel cells should have stopped the development of primary CCS, however, a review of research work only in recent years suggests that primary batteries continue to be improved. The need for energy sources that satisfy a limited set of requirements allowed primary batteries to consolidate their niche in the world market and not give up their positions. Continuing competition motivates to look for ways to get rid of the known shortcomings of primary CCS and to expand the boundaries of their capabilities. In addition to the materials for cathodes and anodes described in this article, as well as electrolytes, attention is drawn to other battery elements. Being sought and new methods of research and new fields of application. Sharper raises the question of recycling; it is logical that it leads to attempts to create more environmentally batteries.

A large number of studies devoted to primary CCS indicates not only how much has been done, but also what remains to be done. All the difficulties and unexpected discoveries open up opportunities for the implementation of new ideas. And these possibilities are, perhaps, endless.

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