

Lithium Ion Batteries: Materials, Products, Market

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Abstract

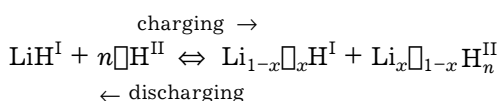
The basic principles of operation of Li-ion batteries (Li-ion) are considered; equations for the electrode potential and charge/discharge kinetics are presented. The most widespread materials for the negative and positive electrodes are described, as well as the composition of electrolytes, their properties and behaviour in Li-ion. The world market and outlooks of the Russian market are analyzed.

THE BASIC PRINCIPLE OF LI-ION OPERATION

Li-ion batteries (Li-ion) are at present the most promising and intensively developing secondary chemical current sources [1]. Having appeared on the market in early 1990s, their production reached 800 mln sp. per year within less than 10 years; they account for more than 60 % (about 5 milliard dollars in the year 2000) of the sales volume of accumulators for household appliances. Structural versions of Li-ion for automobiles, space and military system engineering have been developed and are operating successfully.

Chemical insertion of foreign atoms and molecules (guests) into the lattice of the main material (host) is known since the beginning of the 20th century. The title of the process (insertion) was translated into Latin; since then, they speak not of insertion – extraction but of intercalation – deintercalation (from the Latin word *intercalarius*, or *intercalates*, which means inserted, additional). The reversible conductance of this process by electrochemical method in non-aqueous media, achieved in the second half of the XX century, created experimental basis for the development of a new generation of secondary current sources, *i.e.* lithium-ion batteries. Lithium atom turned out to be main one for which the reversible inter-

calation/deintercalation allowed one to create technologically useful device for accumulation and output of electric energy. Thus, the process was reduced to the transfer of lithium ion through some electrolyte and the transfer of electron through a conductor (containing active load on discharge) from the positive electrode to the negative one (charge) and back (discharge of battery) according to the equation:



where H^{I} , H^{II} are the host matrices of the positive and negative electrodes, respectively, \Box are the vacancies in the crystal structure of the host that are emptied in the positive and occupied in the negative electrode on charging (and *vice versa* on discharging). This fact explains why such an accumulator was initially called rocking chair, later replaced by the name “Lithium ion battery”. Liquid and solid electrolytes are used. Each of them has its own specific features, advantages and shortcomings. Batteries with liquid (Li-ion) and solid (PLi-ion) electrolytes are correspondingly distinguished from each other. This product was first commercialized by Sony company of Japan in the early 1990s.

Below, all the potentials are given with respect to the Li^+/Li reference electrode. Starting from this point, the potential of the intercalant electrode is the emf of the electrochemical circuit $\text{Li}|\text{ADS}, \text{Li}^+ \text{A}^- | < \text{HLi}_x^+ \text{e}^- > | \text{Li}$; it is described by equation [2]

$$E = E^0 + (kT/e) \ln a_{\text{Li}^+}^{\ominus} - (kT/e) \ln a_{\text{Li}^+}^{<\text{H}>} - (kT/e) \ln a_e^{<\text{H}>} = E^0 + (kT/e) \ln \gamma_{\text{Li}^+} c_{\text{Li}^+}^{\ominus} - (kT/e) \ln \gamma_{\text{Li}^+} c_{\text{Li}^+}^{<\text{H}>} - (kT/e) \ln \gamma_e c_e^{<\text{H}>}$$

So, potential of a separate intercalant electrode depends on three variables: the activities of lithium ions in $a_{\text{Li}^+}^{\text{E}}$ electrolyte and in host matrix $a_{\text{Li}^+}^{<\text{H}>}$, and the activity of electrons $a_e^{<\text{H}>}$ in this matrix. This means that such an electrode is principally different from other electrodes for which the equations of potential can be found in [3].

Knowledge of electrode potentials allows calculating thermodynamic functions for intercalant electrode depending on the depth of charge. Results of such a calculation for spectrally pure graphite are shown in Table 1 [4, 5].

Intercalation of a substance into a solid includes two processes of charge transfer through interface: electron transfer (current-carrying material/host matrix) and lithium ion transfer (host matrix/electrolyte), and diffusion distribution over host matrix. The kinetics of intercalation/deintercalation reaction is determined by the diffusion distribution of lithium ions (vacancies) over host matrix, which is the slowest process. Since the diffusion flux is realized inside the solid-phase host matrix, no hindering factors occur, and stable conditions for the development of diffusion transfer processes are created. This allows conducting electrolysis for hours and for months conserving the correct-

ness of conditions for the application of mathematical dependencies developed for chronopotentiometry in electroanalytical chemistry to describe this process [6, 7]. It should be stressed that in this case chronopotentiometry is a diffusion process directed into a solid which takes place in the region near solution.

The particles of electroactive substance in the structure of the electrode are grains of indefinite shape which can be considered in the first approximation as spherical particles. Because of this, in order to analyze the temporal dependencies of potential for charging/discharging separate electrodes of Li-ion, one may use the equation for a reversible process of spherical semi-infinite diffusion [6], as it is considered in chronopotentiometry; the equation can be written as

$$i\tau^{1/2} = 0.5\pi^{1/2}nFD^{1/2}C_{\text{Li}^+} + 0.25\pi nFDC_{\text{Li}^+}\tau^{1/2}/r$$

where i is the electrolysis current density; τ is the transient time, *i. e.* time since the start till the end of electrolysis of a definite electroactive substance; D is the diffusion coefficient of the substance; C_{Li^+} is the concentration of intercalated substance in the host matrix; r is the particle diameter; n is the charge of intercalating particle; F is Faraday number. The first term of this equation takes into account the contribution from linear semi-infinite diffusion, the second one accounts for the contribution due to spherical shape of the electrode [7]. This contribution increases with decreasing current density, decreasing particle radius and increasing concentration of intercalating particles. The effect of contribution from spherical shape of grains manifests itself in the case when $0.25\pi nFDC_{\text{Li}^+}\tau^{1/2}/r$ value becomes comparable or larger than $0.5\pi^{1/2}nFD^{1/2}C_{\text{Li}^+}$; in this

TABLE 1

Thermodynamic functions for carbon electrode depending on charge depth

Function	x values in Li_xC_6				
	0.1	0.17	0.24	0.34	1.0
$-\Delta G$, kJ/mol	205	216	219	227	227
$-\Delta S$, kJ/(mol K)	0.52	0.49	0.42	0.23	0.23
$-\Delta H$, kJ/mol	362	360	346	296	296
dE/dT , mV/K	5.4	5.1	4.4	2.4	2.4

way, the dependence of $i\tau^{1/2}$ on i becomes non-linear.

Calculations indicate that for grain size above 10 μm and current density of the order of several tens milliamperes per gram the effect of spherical shape of grains does not manifest itself till the concentration of intercalating lithium ion corresponding to $x = 1$ in Li_xC_6 and Li_xCoO_2 . This allows considering electrode as a flat plate and describe the kinetics of electrode process by the equation for reversible process, a linear semi-infinite diffusion (Sand's equation) which may be written down as

$$\tau^{1/2} = 0.5\pi^{1/2}nFD^{1/2}C_{\text{Li}^+}/i$$

One can see that $\tau^{1/2}$ is inversely proportional to i , so that the plot is linear in these coordinates.

Expressions for concentration for the cases of reversible and irreversible processes can be substituted in Sand's equation; this gives the dependencies of potential E on transient time τ (which is a constant for a given measurement) and current time of electrolysis t as

$$E = E_{1/2} + (RT/nF)\ln(\tau^{1/2} - t^{1/2})/t^{1/2}$$

for reversible process and

$$E = (RT/\alpha nF)\ln nF C_{\text{Li}^+}k^0/i + (RT/\alpha nF)\ln[1 - (t/\tau)^{1/2}]$$

for irreversible one. Linearization of the experimental data in the coordinates $\lg[(\tau^{1/2} - t^{1/2})/t^{1/2}] - E$ or $\lg[1 - (t/\tau)^{1/2}] - E$ allows attributing an electrode process to the first or to the second case.

Our experimental data indicate that in the major part of cases the process of charging/

discharging of graphite electrodes obeys the equation of linear semi-infinite diffusion for reversible process [5].

Nevertheless, considering an electrode as a flat plane one should take into account the thickness of this plate. In the practice of electrode manufacture for Li-ion, thin plates are used, which can be considered as film-like. The theory of chronopotentiometric process for linear diffusion into a thin film gives the equation:

$$\tau = nFlC_{\text{Li}^+}/i - l^2/3D$$

where l is the thickness of film electrode. Calculation shows that this equation is valid for film thickness less than 0.35 mm for the current of 0.06 mA/cm² and less than 0.17 mm for the current of 0.127 mA/cm². These data correspond to the thickness of film electrodes that are usually used. For the case $l^2/3D_0 \ll \tau$, the second term can be neglected.

A substantial part in the rate of electrode processes is played by diffusion coefficient D . Its values for different electrode materials are listed in Table 2 [8].

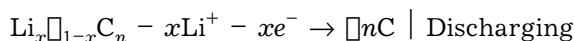
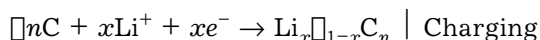
NEGATIVE ELECTRODE

Coke was the first material on the basis of which a commercial sample of Li-ion was made. After that, various modifications of carbon including graphite and carbon based on mesophase initial materials were involved in technological processing.

In this case, the equations of charging/discharging for the negative electrode will be written down as:

TABLE 2
Diffusion coefficient of lithium ion for various carbon materials

Material	Diffusion coefficient, cm ² /g	x region in Li_xC_6	Determination method
Petroleum coke	$1 \cdot 10^{-8} - 1 \cdot 10^{-9}$	$0 < x < 0.65$	PITT
Carbon fiber	$1 \cdot 10^{-10} - 1 \cdot 10^{-12}$	$0 < x < 0.6$	CPR and PSCA
Carbon fiber from tar	$1 \cdot 10^{-10} - 1 \cdot 10^{-11}$	$0.1 < x < 0.5$	EIS
Carbon fiber	$1 \cdot 10^{-6.4} - 1 \cdot 10^{-7.7}$	$0.1 < x < 0.5$	EIS
Artificial graphite	$1 \cdot 10^{-7.7} - 1 \cdot 10^{-8.5}$	$0.1 < x < 0.5$	EIS
Carbon fiber	$1 \cdot 10^{-10}$	$x = 0$	CV models



The theoretical weight specific charge density (specific capacity) of carbon corresponding to these equations is 372 A h/kg; the volume specific charge density is 819 A h/dm³.

Potential realized on uncharged carbon electrode after its manufacture is a random value depending on the set of redox properties of carbon surface and the composition of solution; it can be equal to 2 and 3 V. While charging, the potential shifts to 0 V, which means that the electrode becomes, as it is, lithium one. Within this potential range, both electrolytic decomposition of the components of electrolyte (solvent and salt) and lithium reduction are possible. Multiple repetition of the former and realization of the latter process are unwanted because they are irreversible phenomena.

In the general case, lithium cation occupying vacancies in host structure during intercalation can draw the lattice apart. Reversible operation of the electrode for a long time is possible only if the structure of lattice is fully restored after deintercalation. Lithium ion in solution is solvated and has substantial dimensions. Placing it in the vacancies of carbon matrix during intercalation will lead to substantial strain in carbon crystal structure, which will make the initial crystal structure not restore but get destroyed during deintercalation. One can say that the electrode scales off. Conditions providing elimination of the mentioned processes are determined by choosing the composition of electrolyte.

The Li-ion are assembled in discharged state. Thus assembled battery can be stored however long. It is necessary to charge the battery in order to bring it into the working mode. One can say that the first cycle of charging is pre-sale preparation. This cycle differs substantially in processes on the negative electrode from all the subsequent charging/discharging cycles by the mechanism of the involved phenomena.

Chemical and electrochemical reduction of the solvents for electrolytes, which are esters of carbonic acid (usually ethylene carbonate (EC) and dimethyl carbonate (DC)), is investigated in detail in connection with the problem

of stability of metal lithium in electrolytes containing the mentioned solvents and other aprotic dipolar solvents (ADS) [9]. It is known that the products formed during any procedure of reduction from electrolyte containing lithium ions, on electrode made of any material, including carbon, are identical. One of these products, namely, lithium carbonate, forms a non-porous layer tightly associated with the electrode surface; the author of [10] called this layer a solid electrolyte interface (SEI). Since this title does not take into account the variety of properties of this layer, we proposed [11] to name it insulating polyfunctional layer (IPL). The formation of IPL and destruction of graphite during intercalation of solvate are presented in Fig. 1.

Subsequent behaviour of the carbon electrode is determined by the amount and relation between electronic and ionic conductivity of the material of this layer.

Lithium carbonate (at least in a thin surface layer) is a typical solid electrolyte, *i. e.*, it has rather high ionic conductivity at very small electronic conductivity, no precise values being known for both of them. One may say that this layer possesses the properties of both dielectric (insulator) and solid electrolyte. In the case of metal lithium, this layer is able to provide the currents of anodic dissolution of lithium (due to ionic conductivity) of the order of tens milliamperes, corrosion current (due to electronic conductivity) being of the order of several tenths of microampere. Such a ratio allows assuming that the ionic conductivity

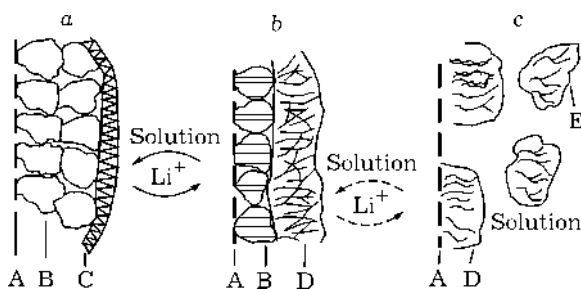


Fig. 1. Schematic description of graphite electrodes in solutions [12]: a - stable, b - partially destroyed, c - destroyed; A - net (current collector), B - active graphite particles, C - compact passivating layer, D - matrix of graphite formed during electrode peeling, and surface particles, E - particles composed of carbon dust and the products of solution reduction.

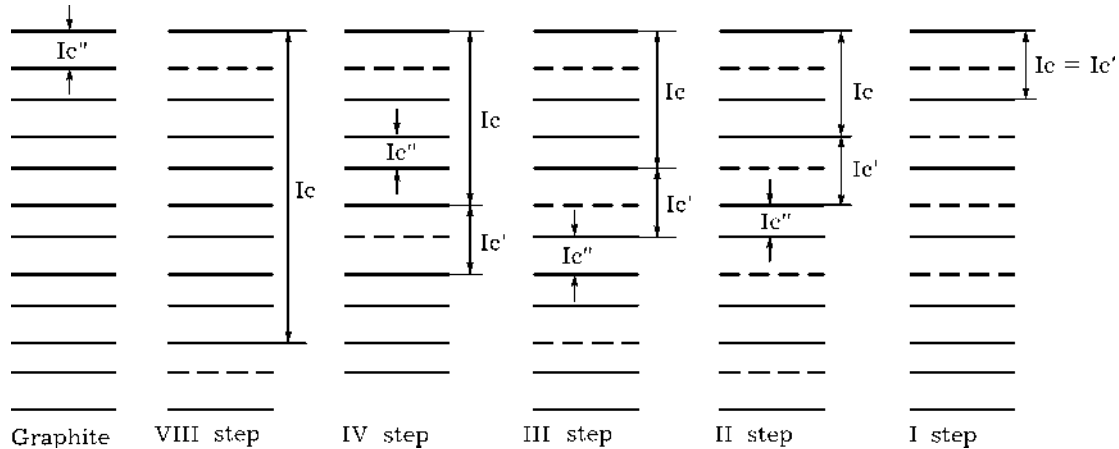


Fig. 2. Distribution of graphite layers (*continuous line*) and lithium (*dash line*) in layered compounds (intercalates) of graphite [14]: Ic – identity period in insertion compounds; Ic' , Ic'' – thickness of the filled and non-filled layers, respectively.

of IPL is ten thousand times higher than the electronic one.

The formation of IPL leads to the cut-off of electron transfer from electrode to electroactive substances in solution; electrolytic reduction of the components of solution stops, and the current passing through the cell is provided only by the transport of lithium ion through OPL into carbon matrix and *vice versa* (during discharging).

Small electronic conductivity of IPL provides good conservation of the electrode charge (small self-discharge).

Compactness of IPL prevents penetration of solvated ions into electrode. Lithium ion is to get rid of its solvate shell before entering IPL; so, desolvated ion enters the carbon matrix for intercalation. Thus, the presence of IPL conserves undestroyed structure of the electrode matrix [12].

A definite amount of electricity is consumed for the formation of IPL during the first charging cycle; this amount is «frozen» in the surface layer and does not return into the circuit during discharging. This phenomenon is called irreversible loss of capacity. Its amount depends on the surface area of the active material, its catalytic properties, and can reach 50 % and more of the reversible electrode capacity. Therefore, for the reversible loss (for LiC_6) equal to 372 A h/kg, the irreversible loss can be 15–200 A h/kg. This fact prescribes definite requirements for designing Li-ion. In order to compensate losses of lithium ions bound in the surface layer during the formation of IPL, it

is necessary to provide an excess of the active material in the positive electrode, which affects specific characteristics of the final product, because the material of the positive electrode accounts for up to 50 % of total cost of Li-ion components.

Attempts are made to decrease irreversible losses of capacity. The level of 50 A h/kg can be achieved by proper choice of carbon. In this respect, pretreatment of the active carbon material by oxidation in ozone-oxygen mixture is promising. Such a treatment allows decreasing irreversible capacity loss by a factor of 2.7 while the reversible discharge capacity increases by 25 % [13].

The structure of the carbon matrix determines thermodynamic and kinetic characteris-

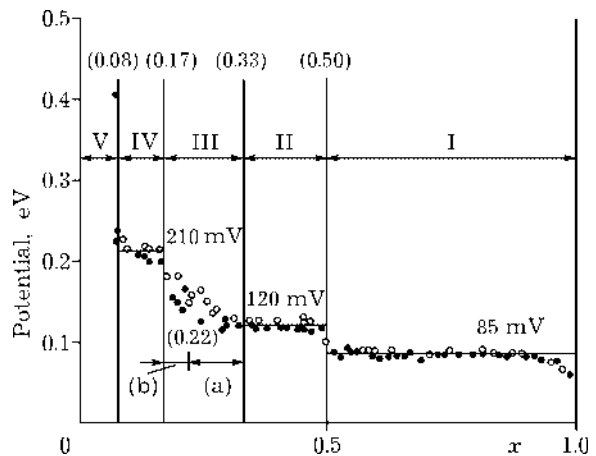


Fig. 3. Dependence of reversible potential of lithium-graphite intercalation compound on the composition x in Li_xC_6 [15].

tics of the carbon electrode. In the case of coke, vacancies in the carbon matrix are close to equivalent ones, and their filling is accompanied by monotonous changes in the electrode potential. In the case of graphite, non-equivalence of separate phase states of the lattice takes place. Non-equivalence results in the fact that both chemical and electrochemical intercalation of lithium into graphite occurs stage-by-stage.

Five steps of lithium insertion into graphite can be distinguished (Fig. 2) [14]. In agreement with this fact, the dependencies on intercalation degree (charge depth) are stepwise: for electrode potential (Fig. 3) [15]; for changes in mean distance between the layers (Fig. 4) [16], which is reflected in XPA spectra (Fig. 5) [17]; charge-discharge curve (Fig. 6) [18]; coefficient of lithium ion diffusion in the host matrix (Fig. 7) [19].

POSITIVE ELECTRODE

The main active material for the positive electrode of Li-ion used at present in commercial products is LiCoO_2 (possibly lithium cobaltate). Physical and electrochemical properties of this compound as cathode material with the ability to cyclic discharging have been de-

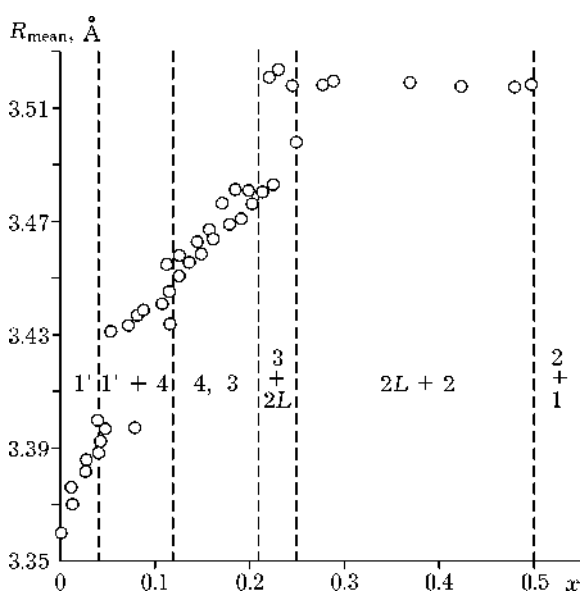


Fig. 4. Changes in mean distance R_{mean} between carbon planes as a function of x in Li_xC_6 . Dash lines show phase diagram [16].

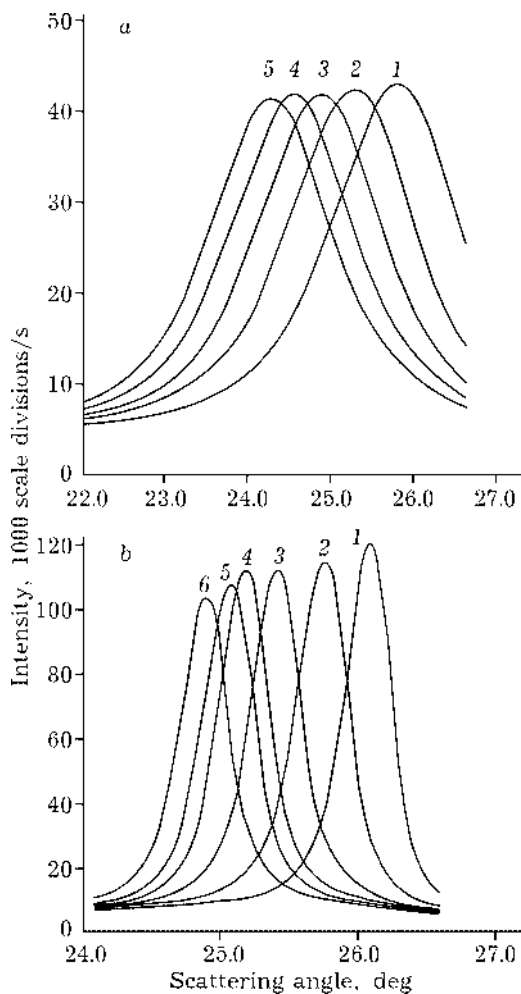


Fig. 5. XPA *in situ* of the (002) region, measured during direct-current discharge of the cell (current corresponds to the change $\Delta x = 1$ in Li_xC_6 for 40 h) [17]: a - Li/petroleum coke; b - the same, heated to 2100 °C; x values: a - 0.005 (1), 0.13 (2), 0.25 (3), 0.37 (4), 0.50 (5); b - 0.005 (1), 0.10 (2), 0.19 (3), 0.28 (4), 0.37 (5), 0.58 (6).

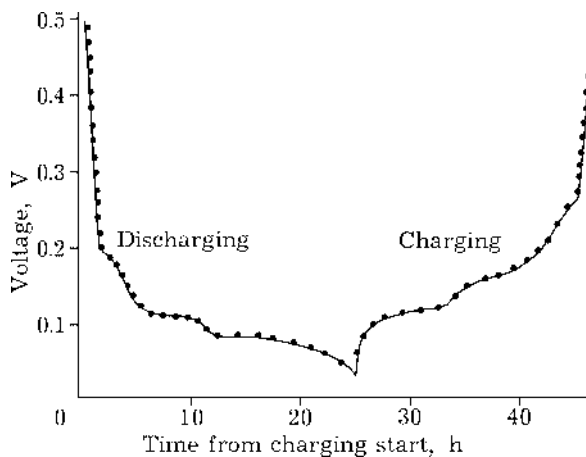


Fig. 6. Charging-discharging curves for the electrode made of graphite. Current density: 15.5 mA/g [18]. Continuous line - cycle 2, points - cycle 19.

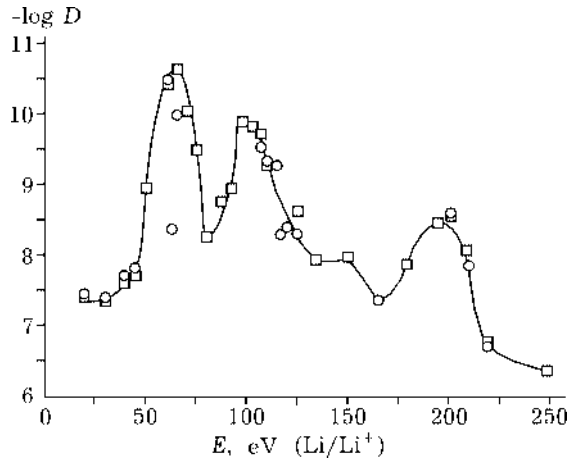
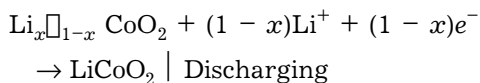
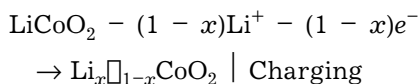


Fig. 7. Dependence of $-\log D$ on E characterizing lithium intercalation into the graphite electrode KS-25 in 1 M LiAsF_6 , ethyl carbonate : dimethyl carbonate = 1 : 3 [19].

scribed for the first time as early as in 1980 [20]. Nevertheless, this material had not attracted attention of technologists in those years, because lithium battery was existing only as a remote perspective and the discharged state of LiCoO_2 compound was not of interest, while the charged (fully reduced) state, *i. e.*, cobalt dioxide, is chemically unstable and cannot be used as cathode material in primary lithium current sources. Attention to this compound arose during the search for a suitable match for carbon anode.

Electrode reactions of lithium cobaltate look like



In agreement with these equations, the theoretical weight specific density of charge (specific capacity) of lithium cobaltate is 274 A h/kg, and the volume specific charge density is 711 A h/dm³.

An idealized structure of lithium cobaltate is shown in Fig. 8 [21]; the dependencies of electrode potentials of lithium cobaltate and nickelate on charge depth are presented in Fig. 9 [22]. (To remind, lithium ion leaves the matrix when the positive electrode is charging.)

X-ray structural data indicate that the oxidation of LiCoO_2 involves two double-phase

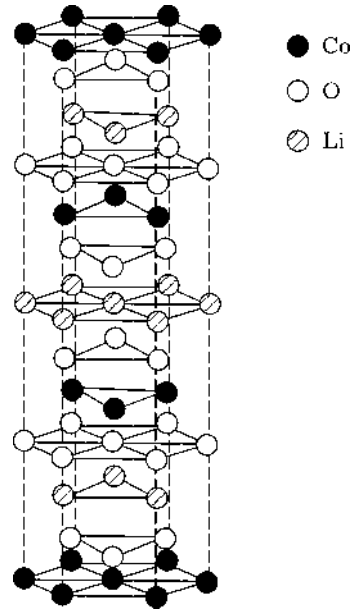


Fig. 8. Idealized structure of LiCoO_2 [21].

reactions in the regions $0 < x < 1/4$ and $3/4 < x < 1$, and one single-phase reaction in the region $1/4 < x < 3/4$. In addition, a fine change of phase occurs near $x = 0.45$. So, the changes in crystal structure occur in the following sequence during charging:

$0 < x < 1/4$, hexagonal + monoclinic, $a = 2.82 \text{ \AA}$, $c = 14.44 \text{ \AA}$

$1/4 < x < 3/4$, monoclinic, $a = 4.91 \text{ \AA}$, $b = 2.82 \text{ \AA}$, $c = 5.02 \text{ \AA}$, $\beta = 111.4^\circ$

$x = 0.45$, monoclinic, $a = 4.90 \text{ \AA}$, $b = 2.81 \text{ \AA}$, $c = 5.05 \text{ \AA}$, $\beta = 108.3^\circ$

$3/4 < x < 1$, hexagonal + monoclinic, $a = 2.82 \text{ \AA}$, $c = 14.26 \text{ \AA}$.

The process of phase change is reversible.

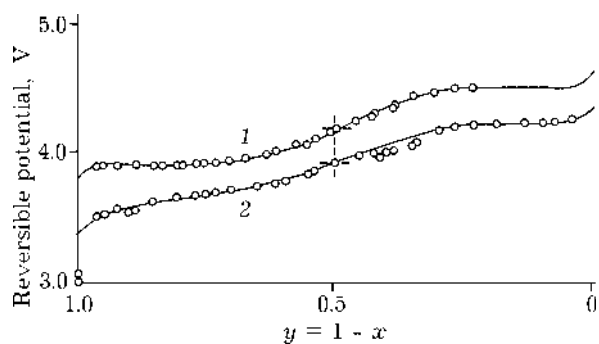


Fig. 9. Comparison between the curves of reversible potential of Li_yCoO_2 (1) and Li_yNiO_2 (2) ($y = 1 - x$) [23].

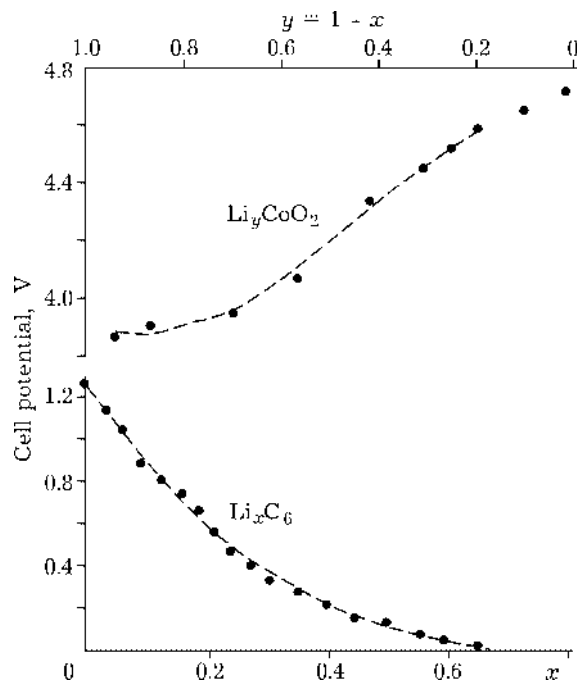


Fig. 10. Change in potentials of separate electrodes of Li-ion during charging [25].

Removal of lithium generates the MO_2 phase, in particular cobalt oxide CoO_2 , with layered structure of CdCl_2 , in which anions form a tightly packed pseudo-cubic matrix.

It should be noted that CoO_2 is thermodynamically unstable under usual conditions. In addition, deintercalation is likely not to proceed till complete removal of lithium from host structure and the final form for the charging of positive electrode is $\text{Li}_{0.067}\text{CoO}_2$ [22].

By summing up the data for the potentials of positive and negative electrodes, the dependence shown in Fig. 10 was obtained [24]. One can see that there are no principal limitations for both the cathode and anode processes, both for charging and for discharging of the battery. During charging, after all the vacancies in carbon matrix are filled (the number of vacancies corresponding to the case when $x > 1$ in Li_xC_6 , as one can see in Fig. 11 [25]), electrode potential will shift to zero and then to the negative side, which will create conditions for the formation of metal lithium. Since lithium is formed in fine state, in which it possesses high reactivity, heat evolved during the interaction of this lithium form with the environment can lead to heat acceleration of reaction and, as a consequence, to depressurization

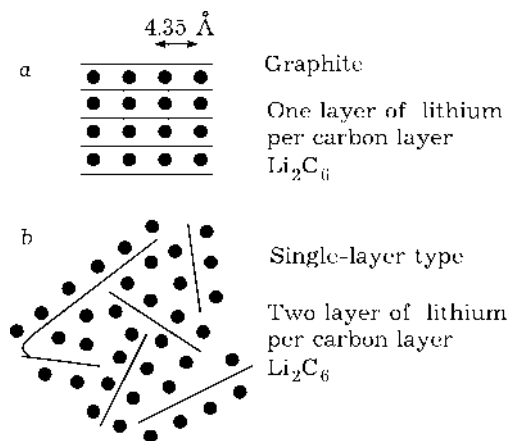


Fig. 11. Schematic representation of lithium intercalation into graphite (a) and a single-layer carbon (b) [24].

of the accumulator. This process is accompanied by the rejection of components of electrode materials and electrolyte, among which lithium cobaltate is of definite danger from the ecological viewpoint (see performance attributes of safety on the site [26], as well as in [1]). To prevent recharging, electronic unit is used in modern models of Li-ion to monitor electrode potentials. This unit stops charging process when the required voltage is achieved by the battery. It should be noted that the introduction of such a unit affects the price of battery (Fig. 12) [31].

One of the promising directions of mastering the properties of active materials is the use of mechanochemical treatment during the synthesis. In application to cathode materials, this direction is successfully developing at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS (Novosibirsk, Russia).

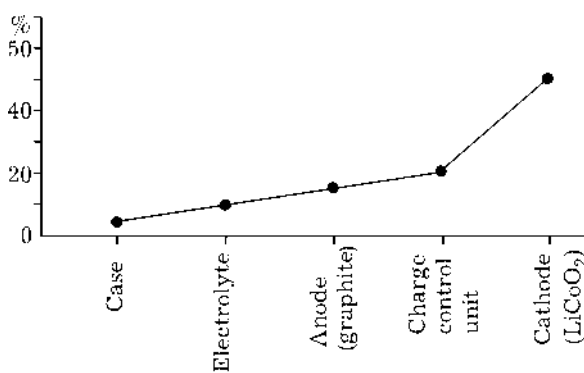


Fig. 12. Structure of factor cost for the production of an averaged unit of Li-ion [31].

Another promising direction is the use of solid-phase amorphization for multicomponent condensed systems in various processes (thermal and mechanochemical action, mechanical alloying, radiation and shock action, *etc.*), which is of fundamental character and can be expressed by a scheme: crystal phases (action) → partial amorphization (action) → new crystal phases. The technological process can be stopped at the stage of partial amorphization using the relaxation principle of governing phase formation; new materials with unusual properties can be thus obtained (for example, with the prescribed exploitation time, with the properties changing with time). An example of achievements in this direction can be the versions of sol-gel method for the synthesis of new forms of active materials, developed at the University of Minnesota (Minneapolis, USA).

ELECTROLYTE

Electrolytes in Li-ion are used to solve two problems.

The first problem, which is mainly traditional for all the chemical current sources, is that electricity is carried in electrolyte only by lithium ion, which is the main reagent in electrode reactions both at the negative and at the positive electrode.

The second problem is perfectly new for current sources; it involves the use of components of electrolyte as reagents for the formation of an insulating polyfunctional layer on the surface of negative electrode performing the described functions.

Two kinds of electrolytes are distinguished: liquid and solid ones. Solvents for liquid electrolytes are esters of carbonic acids, linear (dimethyl and diethyl) and cyclic (ethylene and propylene) carbonates; lithium hexafluorophosphate and/or perchlorate are used as salts. Additives to electrolytes are used as reagents to form IPL other than carbonate, and to protect from overcharging.

By adding chloroethylene carbonate into the electrolyte [27] one can make a chloride (LiCl) layer or, adding SO₂ [28], dithionite layer. Both additives reduce at low negative potentials, which allows using the most widely spread and cheap propylene carbonate as solvent.

In order to provide chemical protection from overcharge, it is proposed to use redox compounds as additives; they consume the excess electricity during overcharge. These additives may be, for instance, aromatic compounds with two methoxy groups both in adjacent and in opposite positions which are stable until 4 V and get oxidized at higher potential. Reversible redox reactions are characteristic of these compounds. This method of protection is called shuttle protection [29].

The major pollutants of electrolytes are atmospheric components: oxygen, nitrogen, carbon dioxide, water. Water plays a special part among them. Lithium hydroxide formed in water reduction possesses comparable ionic and electronic conductivity: $5 \cdot 10^{-14}$ and $>3 \cdot 10^{-15}$, respectively [30], so the surface layer does not possess protective properties. Because of this, the procedures for investigation and for manufacture technology are supplemented with the requirement to provide low level of humidity in the assembled product about 10–100 ppm. All the components of the accumulator are to be thoroughly dried; assembling is to be performed in dry boxes.

Three principally different materials are meant as the solid electrolytes at present. The first one is a polymeric (usually organic) porous matrix impregnated with a liquid electrolyte. The second kind of material includes organic polymeric matrices with inserted (as if dissolved and thus ionized) lithium salts. The third material unites inorganic polymers containing mobile (over vacancies) lithium ions.

MARKET

Three segments of consumers can be distinguished in analyzing the market of Li IA:

1. Branches manufacturing goods of wide usage (portable computers, portable communication means, photo and video technique).
2. Industry (motor-car construction, medicine, means of transport and equipment for railroads, water transport, telecommunication).
3. Branches manufacturing goods of special purpose (space and military engineering, research equipment).

Unbelievable market success of Li-ion is determined by substantial significance of their characteristics in comparison with traditional types of secondary chemical current sources (Table 3).

Production volume

Substantial increase in production volume of home devices equipped with portable sources of electric energy (portable computers, video camera recorders, photo cameras, mobile phones, etc.) predetermined the growth of market of accumulators.

Considering the outlooks of the development of market for each kind of batteries, it is necessary to note that they are not fully interchangeable, so all the kinds will be present in the market in one fraction or another.

For example, though NiCd accumulators have the lowest capacity at the largest overall dimensions, they possess a set of indisputable advantages, for example low cost and the largest number of charging-discharging cycles. This allows predicting conservation of a definite

portion of market to be occupied by these batteries in future.

In addition, the unit of battery charge control, developed in 1996 by SANYO company has drawn the so-called memory effect almost to zero, which explained an overshoot of interest in NiCd accumulators in the second half of the past decade (Fig. 13, a) [31].

Nevertheless, the market of NiCd batteries will shrink; this will be caused mainly not by poor performance characteristics but by the ecological danger connected with the application of this kind of batteries.

NiMH batteries are devoid of the major part of shortcomings characteristic of NiCd batteries, in particular they possess larger capacity at smaller dimensions, which determines substantial growth of their production within the recent three-five years (see Fig. 13, b) [31]. However, such disadvantages as small number of charging-discharging cycles, substantial worsening of discharge characteristics at low temperatures and high self-discharge bring limitations to the application of these batteries and provide the possibility for them to be re-

TABLE 3
Comparative characteristics of batteries of different kinds [31]

Parameter	Type of electrochemical system			
	NiCd	NiMH	Li-ion	PLi-ion
Voltage of element, V	1.25	1.25	3.6	2.7
Energy density, W h/kg	40-60	60-80	100-50	150-200
Energy density, W h/l	150	190	250	370
Number of working cycles of charging/discharging (decrease in capacity by 80 %)	1500	700	1000	150
Internal resistance (for Li-ion at the voltage of 3.6 V), mΩ	100-200	150-250	150-250	No data
Load current	>2 C	(0.5-1.0) C	<1 C	0.2 C
Minimal charging time, h	1.5	2-4	3-4	8-15
Stability to overcharge	Medium	Low	Very low	No data
Self-discharge during a month, %	20	30	1	»
Working temperature range, °C	-40...60	-20...60	-20...60	»
Periodicity of services, days	30	60-90	Not required	»
Price of an averaged unit of product (according to the data by the end of year 2000), dollars per species	0.95	1.3	6.5	»

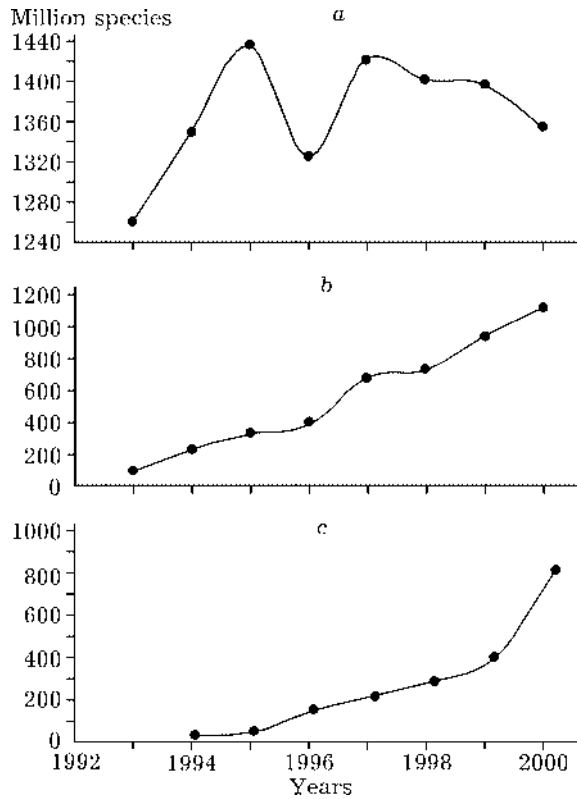


Fig. 13. The dynamics of world production of batteries [31]: a - NiCd, b - NiMH, c - Li-ion.

placed from the market by more progressive chemical current sources (CCS).

At present, Li-ion batteries are the most promising rechargeable CCS. They possess the highest capacity at the smallest dimensions. Their main disadvantage is high cost, which however does not decrease the rate of their advances at the market (see Fig. 13, c) [31].

Growth rate of production volume

The structure and volume of the modern market of Li-ion rechargeable current sources are shown in Table 4.

TABLE 4

Capacity of the market of Li-ion batteries (cut of industrial branches)

No.	Market subsegment	Sales volume, mln sp.		
		1999	2000	2003 (outlook)
1	Goods of general consumption	196	390	576
2	Industrial consumers	128.8	165	278
3	Goods of special consumption	207.5	248.3	412
	<i>Total</i>	532.3	803.3	1266

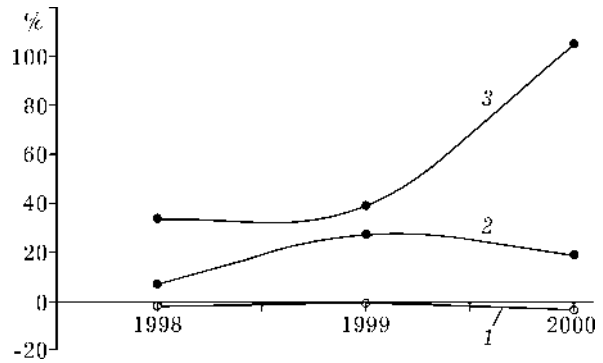


Fig. 14. Growth rate of the production volume of batteries in the world [31]: 1 - NiCd, 2 - NiMH, 3 - Li-ion.

Within the recent three years, the structure of rechargeable current sources distinctly moves toward decreasing fraction of NiCd batteries, increasing fraction of NiMH and Li-ion batteries. The market of NiMH batteries is already close to saturation, which is confirmed by a noticeable decrease in the rates of growth of production and consumption, while the market of Li-ion is, on the contrary, at the rise (the rate of annual growth of production and consumption is 35-40 %, and it exceeded 100 % during the last year (Fig. 14) [31].

So, an increase in the fraction of Li-ion market in the nearest future causes no doubt. This growth will be connected with the replacement of not only NiCd batteries but also NiMH batteries from the market. In the opinion of Gorham experts, the sales volume of Li-ion batteries in 2001 will be more than 900 mln species, while to 2004 it will grow up to 1.3 milliard species per year.

Sales volume

It should be noted that at present the sales volume (in \$ USA) of Li-ion batteries exceeds

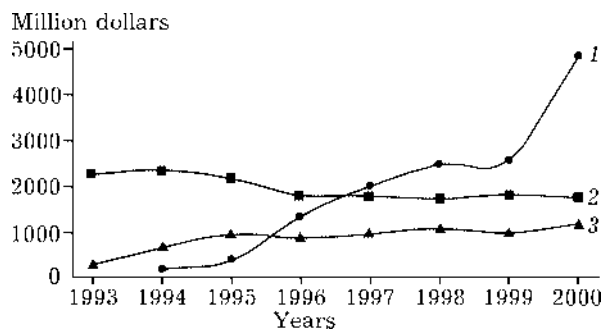


Fig. 15. Sales volume of different kinds of accumulators in the world, in value terms [31]: a – NiCd, b – NiMH, c – Li-ion.

that of NiCd and NiMH batteries taken together (Fig. 15) [31].

So, at present the market of rechargeable current sources is distinguished by high market opportunities, positive dynamics of demand and promising character. A recognized leader on this market is Li-ion accumulator; stable growth of demand for it is predicted by the leading world's analytical and consulting companies for 20–30 future years.

Some outlooks of the application of Li-ion

The world's trend is replacement of other secondary current sources by lithium ion batteries. An estimation of the main constituents of the Li-ion market for the forthcoming years allows making the following conclusions.

Space. Russian manufacturers of satellite systems have already faced the necessity to purchase Li-ion batteries abroad when working on the orders of foreign consumers, since this is a conditions of order. The space branch of Russia is the first-term Russian consumer of Li-ion.

Defense industry. The main result of the military operation of the USA in Afghanistan was that using high-precision weapons and having almost no casualties the American army achieved within 1.5 months what the army of the USSR could not achieve during 10 years of on-land war.

These results define the basic long-term priorities of the world's market of weapons. A good example: in 2001, India has bought defense products for \$2 milliard in Russia and for

\$1 milliard in tiny Israel. Russia sells the weapons of yesterday while our competitors (including Israel) sell up-to-date military products. The use of Li-ion, due to their high performance characteristics, is the basis of energy supply in modern weapons (for example, weapons Tadiran Co., a leader in Israel, has a division specialized for Li-ion developments).

Production of electric bicycles. A new direction in the development of personal transport is the production of electric bicycles, which have entered the market due to the use of Li-ion.

Automobile construction. The world's automobiles industry exhibits three main development trends:

1. Transition to the use of car accumulators with the working voltage of 36–48 V, in order to decrease resistance losses in wires at the conservation of power. Modernization of lead batteries cannot solve this problem because of substantial increase in mass and volume.

2. Development of various hybrid systems that use battery for start, starting run, and a petrol motor operating in a steady mode.

3. Transition to using electric automobiles.

The most acceptable basis for all the three cases is the use of Li-ion. Attempts to realize a hybrid and full electromobile with lead failed because the useful load decreased substantially.

Production of home equipment and devices. This is the most consuming but also the most complicated segment of the market. The development of production inside Russia will make competition a success.

Further progress in the development of lithium ion batteries is closely connected with the characteristics of the active materials used in them; active scientific and technological search is being conducted in this direction.

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