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## INNOVATIVE TECHNOLOGICAL CONCEPT FOR THE PRODUCTION OF HIGH-DENSITY CATHODES FOR LITHIUM RESERVE POWER SOURCES WITH INCREASED SPECIFIC ENERGY

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This paper presents an innovative technological concept that significantly enhances the specific energy (both gravimetric and volumetric) of primary lithium power sources. A composition and laboratory-scale process for manufacturing composite cathodes with minimal electrochemically inactive («ballast») components have been developed. The proposed approach enables the production of high-density cathodes without significantly reducing their porosity. The composite cathodes were tested in disc-shaped primary power sources with dimensions of 2325 (23 mm in diameter and 2.5 mm in height). The effect of graphene content in the cathode mass on the discharge voltage of the cells was investigated. It was demonstrated that a graphene content of 3% by weight of MnO<sub>2</sub> in the cathode mass increases the average discharge voltage of the cells from 2.1 V to 2.5 V at a discharge current of 1 mA. Testing at a discharge current of 1 mA revealed that the capacity of the developed cells exceeds that of the best commercial counterparts by at least 40%.

**Keywords:** lithium power sources, reserve power sources, graphene, MnO<sub>2</sub>, MoO<sub>3</sub>, capacity.

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### Introduction

Developers of lithium and lithium-ion power sources are increasingly focused on improving specific energy, particularly for systems capable of multiple cycling, such as accumulators. This trend is driven by the growing demand in markets for portable electronic devices, electric vehicles, unmanned aerial vehicles, energy storage systems, and other applications. The global lithium-ion battery market, valued at approximately \$60 billion USD today, is projected to grow to \$187 billion USD by 2032.

However, there is a specific range of electronic and electrical devices for which lithium and lithium-ion batteries are unable to meet the operational requirements. For example, the requirements for military reserve batteries were established as early as 1996. These requirements emphasize higher specific energy, low self-discharge, and the inability to recharge

or maintain the power source in a timely manner.

Traditionally, to completely avoid self-discharge, reserve power sources are stored in a dry state without electrolyte. The electrode space is filled with electrolyte only just before the reserve power source is activated. This approach allows the battery to be stored for decades, but at the same time, it prevents immediate deployment. This significantly complicates the design and operational procedures.

Modern lithium-ion batteries offer specific energies up to 250 W·h/kg and self-discharge rates of up to 2% per month. In contrast, reserve power sources with specific energies exceeding 300 W·h/kg have self-discharge rates of less than 1% per year, making them more suitable for long-term applications such as sensors, pacemakers, or other compact, autonomous devices in hard-to-reach areas. Moreover, lithium-based systems are increasingly used in the civilian

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*Innovative technological concept for the production of high-density cathodes for lithium reserve power sources with increased specific energy*

sector due to their versatility.

Primary power sources, which dominate a significant portion of the market, reached a global market value of \$45 billion USD in 2022. This market is projected to grow to \$72 billion USD by 2030, with an average annual growth rate of 6.11%. As such, improving the specific energy performance of batteries across various temperatures and current loads remains a critical goal.

The composition of the cathode layer in primary lithium power sources, with a discharge voltage ranging from 3 to 2 V, typically consists of 80–90% active material, 5–15% conductive additives (such as carbon black or graphite), and about 5–10% polymer binder. In the cathode mass, the carbon material primarily functions as a conductive additive. However, due to its layered structure, the carbon material also aids in the formation and consistency of the electrode mass, which is crucial for meeting the technological and operational parameters of the cathode sheets. That said, the carbon additives and binder do not contribute to the generation of electrical current, making them «ballast» additives. Cathodes produced by using traditional technology have a density of no more than 2.5 g/cm<sup>3</sup>, which limits the specific energy per unit volume.

In the proposed innovative concept, the primary electrochemically active component of the cathode is MnO<sub>2</sub>, and the function of the carbon additive is partially fulfilled by another component with a layered structure. This component is electrochemically active within the working voltage range, while also serving as a conductive additive. Additionally, it contributes to the formation of a high-density cathode layer, which can reach up to 3.5 g/cm<sup>3</sup> without significantly reducing porosity. This is important for ensuring proper discharge of the cathode under increased current. MnO<sub>2</sub> is one of the most widely used electrode materials, not only in primary batteries but also in promising accumulators [1].

In terms of physical and electrochemical properties, the function of this additive can be performed by a number of transition metal oxides, but the most advantageous is MoO<sub>3</sub>. This oxide is a semiconductor with a layered structure, and its conductivity is provided by doping with metal cations of different valences. It is electrochemically active within the working discharge voltage range of the primary cathode component, has a high density (4.75 g/cm<sup>3</sup>), is non-toxic, and is relatively inexpensive. The galvanostatic curve profile of this oxide is characterized by two plateaus at 2.75 and 2.3 V relative to a Li reference electrode. These values fall within the 3.0 to 2.0 V range, which is the working

discharge voltage range of MnO<sub>2</sub>-based cathodes. During discharge, stoichiometric MnO<sub>2</sub> is transformed into a non-stoichiometric structure of lithium-intercalated oxide bronze Li<sub>x</sub>MoO<sub>3</sub>, whose electronic conductivity increases with the amount of intercalated lithium. This, in turn, enhances the overall electronic conductivity of the cathode layer and increases the discharge voltage under high current loads.

However, to implement this concept, it is necessary to ensure the initiation of discharge with the current required by the consumer. The issue is that both MnO<sub>2</sub> and MoO<sub>3</sub> are semiconductors with low electronic conductivity and significant resistance at the phase boundary between these oxide materials. Cathodes made solely from oxides do not provide the necessary discharge current. Therefore, the key idea behind this concept is to reduce the phase boundary resistance between MnO<sub>2</sub> and MoO<sub>3</sub> by modifying the surface of MnO<sub>2</sub> particles with a conductive material. At the same time, the amount of such material must be minimal to avoid negatively affecting the specific weight of the cathode layer. Graphene is nearly ideal for this surface modification.

The most well-known analogue of this type of hybrid cathode material for lithium power sources is the MnO<sub>2</sub>-CF<sub>x</sub> composite [2,3]. The synergistic effect at the phase boundary between MnO<sub>2</sub>, CF<sub>x</sub>, and the electrolyte leads to increased specific energy, raises the average discharge voltage, and reduces the voltage drop at the beginning of discharge [4]. This type of cathode material is used in commercial cylindrical power sources manufactured by Ultralife.

MnO<sub>2</sub> and MoO<sub>3</sub> composites have attracted interest as anode materials for lithium-ion batteries [5]. The initial specific capacity of such anodes is 2333.1 mA·h/g, but it decreases to 908.8 mA·h/g after 50 cycles. It is noted that anodes based on this composite operate in the potential range of 3.0 to 0.01 V. Unlike the composite presented in this work, which is intended for use as a cathode material, these composites are not used in lithium power sources.

MoO<sub>3</sub> was previously used as a cathode material in commercial power sources, but recently molybdenum (VI) oxide has found applications in lithium-ion systems [6,7]. It has been noted that modifying NMC cathodes with this oxide for lithium-ion batteries is promising, where the MoO<sub>3</sub> coating plays a key role in inhibiting structural degradation and absorbing HF, which prevents an increase in charge transfer resistance and enhances electrochemical performance [8].

#### **Materials and methods**

Cathodes were manufactured by mixing MnO<sub>2</sub> powders (HDM  $\gamma$ - $\beta$  modification, particle

size  $<40\ \mu\text{m}$ ) with graphene in amounts ranging from 1% to 3% of the  $\text{MoO}_3$  mass. Graphene was uniformly distributed over the surface of the  $\text{MnO}_2$  particles.

Graphene with a «pom-pom» structure (Fig. 1) was used in this work, which had previously been successfully applied as an additive to the cathode mass of a lithium-sulfur battery [9].

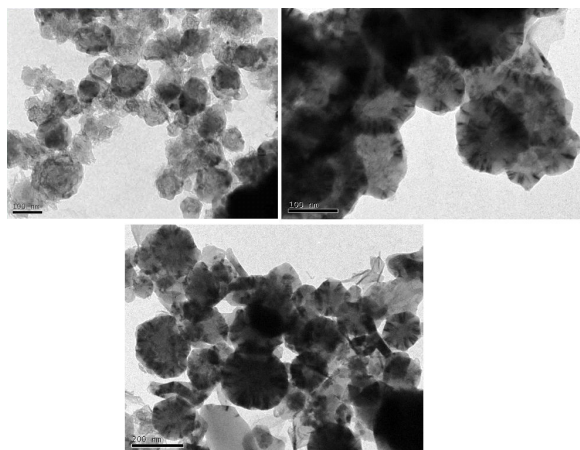


Fig. 1. TEM images of graphene with a «pom-pom» structure

After adding  $\text{MoO}_3$  powder (chemically pure grade) to the mixture, a composite was formed in which the  $\text{MnO}_2$  and  $\text{MoO}_3$  phases contacted through the graphene phase, significantly reducing the resistance at the phase boundary between the two oxides.

After mixing, a fluoropolymer-based binder was added to the dry component mixture in an amount of up to 1% of the total cathode mass. The resulting cathode mass was mixed and dried at  $60^\circ\text{C}$  for 24 hours. After drying, the cathode mass was ground in a high-speed grinder. The crushed cathode mass was pressed onto the current collector of the disc element using a press mold. The diameter of the cathode is 18 mm, and the pressing force was 2.4 tons on the entire cathode. After manufacturing, the cathode underwent thermal treatment for 4 hours at  $250^\circ\text{C}$ . The density of the cathode layer based on the composite  $\text{MnO}_2/\text{MoO}_3$  cathodes reached  $3.5\pm 0.05\ \text{g}/\text{cm}^3$ .

The anode was made from metallic lithium of grade LE-1. To reduce the resistance at the lithium/electrolyte interface, the lithium surface was modified with a Li-Al alloy. The thickness of the modification layer was 3–5  $\mu\text{m}$ .

The cathodes were tested in disc-shaped elements of size 2325 under the condition that the electrochemical capacity of the cathode equaled the electrochemical capacity of the lithium anode.

The thickness of the electrode structure (cathode, anode, and separator) was selected so that the element's

thickness in the discharged state did not exceed the specified dimension (2.5 mm for size 2325). The weight of the cathode was  $1.0\pm 0.01\ \text{g}$ , with a thickness of  $1.2\pm 0.003\ \text{mm}$ . The weight of the anode was  $0.08\pm 0.003\ \text{g}$ , with a thickness of  $0.65\pm 0.01\ \text{mm}$ .

As an aprotic electrolyte, a 1 M solution of  $\text{LiClO}_4$  in a solvent mixture of propylene carbonate and dimethoxyethane (3:1 by volume) was used. Before use, the electrolyte was dried over freshly calcined molecular sieves (4 Å). The water content in the prepared electrolyte was less than 100 ppm.

Galvanostatic studies were conducted by discharging the assembled disc elements with a discharge current of 1 mA at a temperature of  $+25^\circ\text{C}$ . The final discharge voltage ranged from 2.0 to 1.8 V.

### Results and discussion

The discharge profile of the 2325 form factor elements with a graphene content of 1% (relative to the total  $\text{MnO}_2$  content) is presented in Fig. 2.

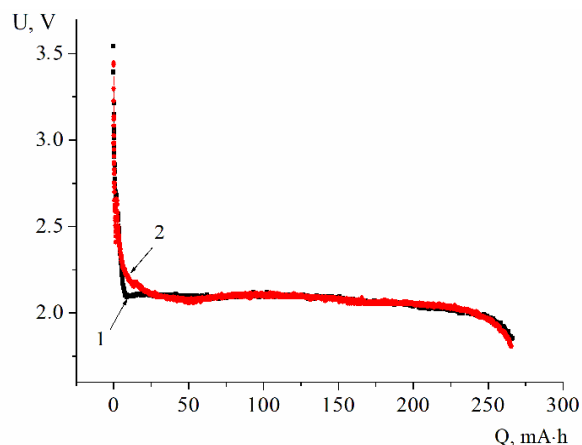


Fig. 2. Discharge characteristics of 2325-sized elements with a composite  $\text{MnO}_2:\text{MoO}_3$  (50:50) cathode. The amount of graphene in the cathode mass is 1% of the  $\text{MnO}_2$  content.

Discharge current is 1 mA. Curve 1 corresponds to the element No. 21; curve 2 corresponds to the element No. 34

As seen in Fig. 2, the average discharge voltage of the elements with 1% graphene content in the cathode mass (relative to the  $\text{MnO}_2$  content) is relatively low, around 2.1 V. This indicates that this amount of graphene does not effectively reduce the resistance at the phase boundary between manganese and molybdenum oxides across the entire contact surface of the composite structure. It is also worth noting that the discharge profile of the composite cathode exhibits a single plateau, even though the electrochemical reduction of  $\text{MnO}_2$  and  $\text{MoO}_3$  during lithium-ion intercalation occurs at different potentials. The capacity of the elements with 1% graphene is quite high, around 270 mA·h per gram of cathode

material, with the utilization rate of the cathode materials approaching 90%.

Increasing the graphene content in the cathode mass to 3% of the  $\text{MnO}_2$  content leads to a significant change in the cathode profile. Figure 3 shows typical discharge curves for 2325-sized elements with cathodes containing an increased amount of graphene.

Increasing the graphene content in the cathode mass to 3% of the  $\text{MnO}_2$  content raises the average discharge voltage of the elements to 2.4 V. The increased contact area between the  $\text{MnO}_2$  and  $\text{MoO}_3$  phases through the graphene phase revealed at least three plateaus (2.8 V, 2.4–2.5 V, and 2.2 V) on the discharge curves, corresponding to the electrochemical reduction processes of manganese dioxide and molybdenum trioxide.

The discharge capacity of the elements (Fig. 3) averages ~275 mA·h at a discharge current of 1 mA, which is more than 40% higher than the best-known commercial products (such as 190 mA·h for Duracell elements).

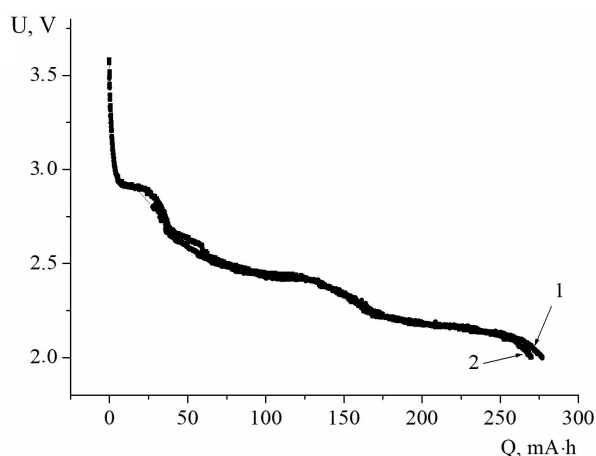


Fig. 3. Discharge characteristics of 2325-sized elements with a composite  $\text{MnO}_2$ : $\text{MoO}_3$  (50:50) cathode. The amount of graphene in the cathode mass is 3% of the  $\text{MnO}_2$  content.

Discharge current is 1 mA. Curve 1 corresponds to the element No. 58; curve 2 corresponds to the element No. 59

Table provides a comparison of the main characteristics of 2325-sized elements from global manufacturers and the innovative elements with

$\text{MnO}_2$ / $\text{MoO}_3$  composite cathodes. Information on the characteristics of Panasonic and Duracell elements is taken from the promotional brochures of these manufacturers.

The advantage of the elements based on the innovative  $\text{MnO}_2$ / $\text{MoO}_3$  composite cathodes, compared to commercial counterparts, is particularly evident in their energy performance (Fig. 4).

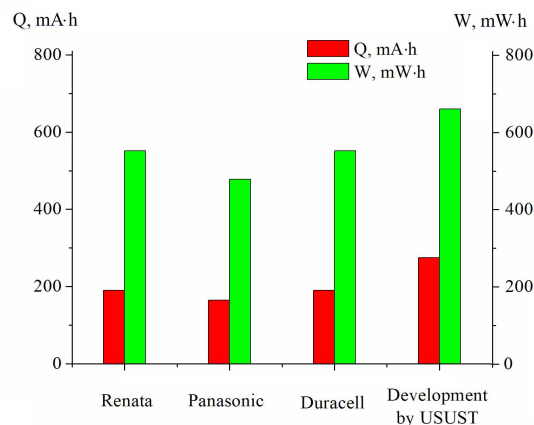


Fig. 4. Comparison diagram of capacity and energy of 2325-sized elements

As shown in Fig. 4, the energy of 2325-sized elements from commercial manufacturers Renata and Duracell (with a maximum capacity of 190 mA·h) is 550 mW·h. In comparison, the energy of the prototype elements with  $\text{MnO}_2$ / $\text{MoO}_3$  composite cathodes is 660 mW·h, which is approximately 20% higher than that of the commercial elements.

### Conclusions

1. An innovative technological concept for producing composite cathodes with up to 98% electrochemically active material and ultra-high cathode layer density (up to 3.5 g/cm<sup>3</sup>) has been developed.

2. It has been shown that increasing the graphene content from 1% to 3% of the  $\text{MnO}_2$  in the cathode mass raises the average discharge voltage of the cells from 2.1 V to 2.4 V at a discharge current of 1 mA. The combination of physical and electrochemical properties in the 2325 form factor resulted in a 40% increase in capacity and a 20% boost in energy output

### Comparison of the main characteristics of 2325-sized elements

Indicator	Values for different manufacturers			
	Renata	Panasonic	Duracell	Development by USUST
cathode active material	$\text{MnO}_2$	CFx	$\text{MnO}_2$	$\text{MnO}_2$ / $\text{MoO}_3$ composite
voltage, V	3.0 (2.9)	3.0 (2.9)	3.0 (2.9)	2.4
capacity, mA·h	190	165	190	275
maximum discharge current, mA	3.0	–	–	1.0



compared to commercial products from well-known manufacturers.

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## ІННОВАЦІЙНА ТЕХНОЛОГІЧНА КОНЦЕПЦІЯ ВИГОТОВЛЕННЯ КАТОДІВ З ВИСОКОЮ ЩІЛЬНІСТЮ ДЛЯ ЛІТІЄВИХ РЕЗЕРВНИХ ДЖЕРЕЛ ЖИВЛЕННЯ З ПІДВИЩЕНОЮ ПИТОМОЮ ЕНЕРГІЄЮ

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Надано інноваційну технологічну концепцію, застосування якої радикально підвищує питому енергію (на одиницю ваги та об'єму) первинних літєвих джерел струму. Розроблено склад і лабораторну технологію виготовлення композитних катодів, які практично не містять баластних (електрохімічно пасивних) компонентів. Застосування запропонованої концепції дозволяє виготовляти катоди високої щільності без суттєвого зменшення їх пористості. Композитні катоди були протестовані у дискових первинних джерелах живлення в габаритах 2325 (діаметр 23 мм, висота 2,5 мм). Досліджено вплив вмісту графену у складі катодної маси на розрядну напругу елементів. Показано, що вміст графену 3% від вагової долі MnO<sub>2</sub> в катодній масі підвищує середню розрядну напругу елементів з 2,1 до 2,5 В при струмі розряду 1 мА. Випробування елементів при струмі 1 мА показало, що при розряді до кінцевої напруги 2 В їх ємність перевищує ємність кращих комерційних аналогів мінімум на 40%.

**Ключові слова:** літєві джерела струму, резервні джерела живлення, графен, MnO<sub>2</sub>, MoO<sub>3</sub>, ємність.

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