**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program 8D05301 – Chemistry

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# Study on electrolytes for chemical power sources with a lithium anode

**General overview of the work**

In the present dissertation, electrolyte systems for chemical power sources with a metallic lithium anode and anode-free configurations based on various lithium salts and organic solvents were investigated. Special attention was paid to the influence of functional additives on the electrochemical performance of the cells. It was established that the electrolyte composition governs the processes of interfacial layer formation, the stability of the lithium electrode, and the electrochemical characteristics of cells in different systems. For each type of lithium-based power source, optimal electrolyte compositions were identified that provide the best combination of specific capacity, long-term stability, and coulombic efficiency.

**Relevance of the research topic**

In recent years, the demand for lithium-based chemical power sources has increased significantly due to their high energy density and long service life. However, their main limitation remains the instability of metallic lithium at the anode. Direct contact of lithium with organic electrolytes leads to solvent decomposition, formation of an unstable and high-resistance solid electrolyte interphase (SEI), and dendrite growth. These phenomena result in capacity fading, deterioration of coulombic efficiency, increased risk of internal short circuit, premature device failure, and safety issues.

Therefore, the development of electrolytes capable of ensuring stable lithium operation and efficient lithium-ion kinetics under various operating conditions remains a key challenge in electrochemical power source technology. In particular, electrolyte systems that promote the formation of a stable SEI layer while maintaining high ionic conductivity over a wide temperature range are of special interest.

Despite extensive research, systematic comparative studies of electrolyte salt–solvent combinations in terms of ionic conductivity, SEI resistance, and cycling stability for both primary and secondary lithium systems remain limited. At the same time, the growing demand for reliable lithium power sources in medical, defense, and autonomous electronic devices requires stable operation over a wide temperature range without performance degradation. Technological compatibility with existing cell formats is also important for industrial implementation without large-scale equipment modernization.

For Kazakhstan, the development of such systems directly contributes to technological independence, the advancement of green energy and electromobility, and diversification of high-tech exports.

In this regard, the present dissertation is aimed at identifying optimal electrolyte compositions that stabilize the lithium anode and ensure reliable electrochemical performance, thereby addressing both fundamental interfacial processes and practical application requirements. The work contributes to solving the fundamental problem of

lithium metal stabilization and has significant scientific and practical relevance for modern energy storage technologies.

**Aim of the Dissertation**

The aim of the dissertation is to develop scientifically substantiated approaches to the selection and optimization of electrolyte compositions for chemical power sources with a lithium anode, ensuring high ionic conductivity, the formation of a stable and low-resistance solid electrolyte interphase (SEI), as well as long-term electrochemical stability and efficiency of cells under various operating conditions and temperature ranges.

To achieve this aim, the following **objectives** were set in the study:

1. Selection and preparation of electrolyte systems;
2. Investigation of the influence of electrolyte compositions on the stability of the lithium electrode during cycling;
3. Study of the interfacial layer formed on the surface of the lithium electrode during cycling;
4. Investigation of the effect of electrolyte composition on electrochemical properties;
5. Assembly of a prototype chemical power source using lithium metal as the anode and evaluation of its performance.

**Object of the Study**

The object of the study comprises electrolyte systems for chemical power sources with a lithium anode based on the salts LiDFOB, LiTFSI, $LiBF_4$, $LiClO_4$, and $LiPF_6$ in mixtures of propylene carbonate (PC), dimethoxyethane (DME), fluoroethylene carbonate (FEC), and ethyl acetate (EA), with the addition of 1,3-dioxolane (DOL), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and $LiNO_3$.

**Subject of the Study**

The subject of the study is the influence of electrolyte composition (the nature of lithium salts, solvent mixtures, and functional additives) on the processes of interfacial layer formation, the stability of the lithium electrode, cycling behavior, and electrochemical characteristics of various types of chemical power sources (Li-$V_2O_5$, Li-$CF_x$, Li-$CF_x$/$V_2O_5$, Cu-$NMC_{111}$).

**Research Methods**

In the present dissertation, a comprehensive set of methods was employed to investigate electrolyte systems, including both electrochemical and physicochemical approaches. Electrochemical testing was carried out using galvanostatic cycling to evaluate specific capacity, stability, and cycle life of the cells, as well as to record discharge profiles under various current regimes and determine coulombic efficiency. Electrochemical impedance spectroscopy was applied in the frequency range from 100 kHz to 10 mHz to analyze interfacial resistance, charge transfer processes, and ionic conductivity. Scanning electron microscopy was used to analyze the structure and morphology of electrode surfaces. Within the framework of prototyping, lithium cells of various types were assembled in an argon-filled glove box using standard laboratory equipment, and prismatic prototype cells in laminated aluminum foil soft packaging were fabricated.

**Scientific Novelty**

For the first time, a comprehensive study was carried out on the influence of electrolyte composition – the nature of the lithium salt, solvent mixtures, and functional additives – on the set of performance characteristics of two main types of lithium chemical power sources. These characteristics include ionic conductivity, charge-transfer resistance, and SEI layer stability:

- Secondary power sources (Li– $V_2O_5$, Cu–$NMC_{111}$),
- Primary power sources (Li–$CF_x$, Li–$V_2O_5/CF_x$).

For electrolytes based on LiDFOB, LiTFSI, $LiBF_4$, $LiClO_4$ and $LiPF_6$ salts in PC:DME, FEC:DME, and PC:DME:EA solvent mixtures with DOL, FEC and $LiNO_3$ additives, the temperature dependences of ionic conductivity were systematically obtained for the first time in the range from −20 °C to 60 °C.

It was demonstrated that the use of 1 M LiDFOB in PC:DME with 2% FEC + 2% VC forms a hybrid SEI enriched with LiF and VC polymerization products, which significantly reduces interfacial resistance, increases coulombic efficiency to 99–100%, and ensures high capacity retention at high current loads in Li–$V_2O_5$ systems.

LiDFOB electrolytes containing DOL additive form an elastic and robust SEI layer under high current loads (capacity retention up to 120–140 mAh/g at 5C), improving rate capability. In contrast, LiTFSI-based systems exhibited the highest long-term stability at low and medium current regimes (C/2–C), maintaining ~100 mAh/g for nearly 300 cycles with 99–100% coulombic efficiency. Thus, LiDFOB electrolytes are optimal for high-rate operation, whereas LiTFSI is preferable for long cycle life.

Differences in SEI nature were identified: in LiDFOB-based electrolytes the SEI possesses a boron-organic structure, explaining high stability at low temperatures and distinctive high-rate discharge behavior; in LiTFSI-based systems a thin inorganic LiF-rich SEI is formed, ensuring high-power performance.

Optimal electrolyte compositions were proposed for different systems:

- For Li– $V_2O_5/CF_x$ systems – 1 M LiTFSI in PC:DME (3:7) + 15% DOL;
- For Li– $V_2O_5$ systems – 1 M LiDFOB in PC:DME (3:7) + 2% FEC + 2% VC;
- For Li–$CF_x$ systems – 0,4 M LiDFOB + 0,6 M $LiBF_4$ in PC:DME (3:7);
- For anode-free Cu–$NMC_{111}$ systems – electrolytes based on LiDFOB and $LiPF_6$ salts in FEC:DME solvent mixture.

For the first time, prismatic cell prototyping was performed using 1 M LiTFSI in PC:DME + 15% DOL electrolyte and a $V_2O_5/CF_x$ hybrid cathode, achieving specific energy up to 420 Wh/kg while maintaining stable operation under high-rate conditions.

**Key provisions for defense**

1. It was established that an electrolyte based on 1 M LiTFSI salt dissolved in a PC:DME solvent mixture (3:7) with 15% DOL additive ensures the formation of an elastic, stable, and low-resistance interfacial layer (SEI) on the lithium anode in the Li–$V_2O_5$ system. This is confirmed by a 10–15% decrease in interfacial resistance according to impedance spectroscopy data, achieving a coulombic efficiency of 99–100% in the initial cycles, and maintaining a capacity of about 100 mAh/g for ~300 cycles.
2. It was established that in the anode-free Cu–NMC111 system, an electrolyte based on 1 M LiDFOB salt in an FEC:DME solvent mixture achieves a specific capacity of ≈200 mAh/g and a coulombic efficiency of ≈96% at 30 °C. At 60 °C, stable

electrochemical characteristics of the system are preserved. The electrolyte composition exhibits high ionic conductivity in the temperature range −20–60 °C. The stable retention of coulombic efficiency during cycling indicates the formation of a stable interfacial layer on the copper surface and a reduction in the intensity of side reactions.

3. A dual-salt electrolyte of 0,4 M LiDFOB + 0,6 M $LiBF_4$ in a PC:DME (3:7) solvent mixture is used in Li–$CF_x$ primary cells under low-temperature conditions. The electrolyte provides a stable discharge plateau in the range of 2,2–1,9 V and a specific capacity of ≈230 mAh/g at −20 °C. It is demonstrated that, compared with the studied single-salt electrolytes, the use of the dual-salt electrolyte improves the low-temperature electrochemical performance of primary cells.

**Practical and theoretical significance of the work**

The practical significance of the dissertation lies in the possibility of direct application of the developed and optimized liquid electrolyte compositions for lithium-anode-based electrochemical power sources. The comprehensive study identified optimal electrolyte formulations providing high ionic conductivity, formation of a stable solid interphase layer, and low interfacial resistance. These parameters are crucial for improving energy efficiency, long-term stability, and overall reliability of the cells.

The proposed electrolyte compositions are based on commercially available reagents and are technologically compatible with CR2032 cells as well as pouch-type batteries, enabling their direct industrial implementation. The developed methodology for evaluating the suitability of new electrolyte can be applied both in quality-control laboratories of battery manufacturing enterprises and in research laboratories. For the Republic of Kazakhstan, the results are of practical importance for the development of energy storage systems, stabilization of renewable energy sources, and reduction of import dependence in battery technologies.

The theoretical significance of the work consists in establishing the regularities of the influence of electrolyte composition on interfacial processes at the lithium anode surface, the structural features of the SEI layer, and charge-transfer kinetics. The influence of lithium salt nature and functional additives on interfacial resistance ($R_{SEI}$), charge-transfer resistance ($R_{ct}$), and ionic conductivity was quantitatively substantiated. The obtained data clarify the mechanisms of impedance response formation in systems with lithium metal anodes and provide deeper understanding of physicochemical processes at the electrode–electrolyte interface, forming a basis for improving theoretical models in electrolyte chemistry and interfacial electrochemistry.

**The accuracy of the obtained results** was ensured through the use of modern instrumental methods, which made it possible to reproduce the experimental data with minimal errors.

**Approbation of the results of the dissertation work**

The practical results of the dissertation have been presented and validated at international and national scientific conferences:

- International Scientific and Practical Conference “XVII Toraighyrov Readings” (Pavlodar, 2025);
- International Scientific Conference “11th Polish–Kazakh Meeting” (Poland, 2025);
- International Scientific Conference “Science and Industry: Challenges and Opportunities” (Lublin, 2024);

- International Scientific Conference of Students and Young Scientists “Farabi Álemi” (Almaty, 2024);
- International Scientific Conference “9th Polish–Kazakh Meeting” (2023);
- International Scientific Conference “Modern Achievements and Trends in Chemistry and Chemical Technology in the 21st Century” (Pavlodar, 2023).

**Publications**

Based on the results of the dissertation research, 12 publications have been produced, including**:**

- 4 articles published in journals recommended by the Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan;
- 1 article published in a peer-reviewed journal indexed in the Scopus database;
- 6 conference abstracts presented at international scientific conferences;
- 1 utility model patent of the Republic of Kazakhstan.

**Description of the doctoral student's contribution to each publication**

Abdrakhmanova A., Sabitova A., Mussabayeva B., Bayakhmetova B., Sharipkhan Z., Yermoldina E. Investigation of Ionic Conductivity of Electrolytes for Anode-Free Lithium-Ion Batteries by Impedance Spectroscopy // Electrochem. MDPI AG. – 2025. – Vol. 6, Iss. 20. – P. 20: research, methodology, validation, visualization, writing – original draft, editing.

Abdrakhmanova A., Omarova N., Sabitova A., Kuderina B. Low- Temperature Electrochemical Behavior of $Li/CF_x$ Cells: The Role of Electrolyte Composition. // Bulletin of the L.N. Gumilyov ENU. Chemistry. Geography Series. – 2025. – Vol. 153, Iss. 4. – P.11-19: research, methodology, validation, visualization, writing – original draft, editing.

Abdrakhmanova A., Krivchenko V., Sabitova A., Kuderina B. DOL-Enhanced Electrolytes As a Route to Stable Anodes in $Li\text{-}V_2O_5$ Systems // Academic Journal Of Physical And Chemical Sciences. – 2025. – Vol 4, Iss. 356. – P.196-207: research, methodology, validation, visualization, writing – original draft, editing.

Абдрахманова А., Омарова Н., Сабитова А. Влияние состава электролитов на электрохимические показатели безанодных литий-ионных элементов // доклады национальной академии наук РК. – 2023. – Т. 3, № 347. – Р. 83–93: research, methodology, validation, visualization, writing – original draft, editing.

Abdrakhmanova A., Sabitova A., Omarova N. A review on electrolytic systems for lithium-ion batteries // News of the national academy of sciences of the Republic of Kazakhstan. – 2023. – Vol. 3, Iss. 456. – P. 7–21: research, methodology, validation, visualization, writing – original draft, editing.

**Structure and Scope of the Dissertation**

The dissertation consists of three chapters, a conclusion, a list of references comprising 164 published sources an appendix. The main body of the dissertation is presented on 129 pages and is illustrated with 34 figures and 6 tables.