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Boron-Doped $LiCoPO_4$ as a High-Voltage Cathode for Lithium-Ion Batteries

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ABSTRACT

The primary aim of this work is to demonstrate the influence of boron doping on $LiCoPO_4$ (LCP) cathodes with a focus on conductivity and interfacial processes. Pristine and B-doped LCP were synthesized via a two-step solid-state method. XRD and SEM confirmed phase purity, lattice distortion and reduced particle size in the doped sample. Electrochemical impedance spectroscopy showed improved lithium-ion diffusion, higher coulombic efficiency (to ~75% vs. ~65%) and moderate capacity retention for the doped sample (~60 $mAh \cdot g^{-1}$ after 20 cycles) compared to pristine LCP. These findings highlight that boron doping effectively enhances conductivity and mitigates interfacial limitations of LCP, providing a promising, but still preliminary strategy for the development of high-voltage LIBs cathodes.

1. Introduction

The rapid advancement of energy storage technologies is essential to meet the growing demand for efficient, sustainable power sources [1-3]. Lithium-ion batteries (LIBs) have become the dominant solution due to their high energy density, long cycle life, and excellent electrochemical stability [4, 5]. However, the widespread use of layered oxide cathodes, such as $LiCoO_2$ (LCO), is challenged by safety concerns, cost, and resource limitations [5], prompting the search for alternative materials. Olivine-types phosphates, $LiMPO_4$ (M = Fe, Mn, Co, Ni), have attracted significant attention due to their strong structural framework, thermal stability, and well-defined redox potentials [6-13]. $LiCoPO_4$ (LCP), first reported by Amine et al. [13], operates at high voltage 4.8 V vs. Li/Li^+ and has a theoretical capacity of 167 $mAh \cdot g^{-1}$ with high energy density (~800 $Wh \cdot kg^{-1}$) [14]. Phosphate-based cathodes provide superior thermal safety due to strong P–O covalent bonding [15-17]. However, LCP suffers from poor electronic conductivity (~10^{-9} $S \cdot cm^{-1}$), sluggish lithium-ion diffusion, and electrolyte decomposition at high voltages [18, 19].

To overcome these limitations, strategies such as elemental doping are being explored. Boron (B) doping has been shown to enhance electrical conductivity, structural stability, and lithium-ion diffusion [20, 21]. This study investigates how boron incorporation affects the structural, morphological, and interfacial electrochemistry of LCP, enhancing conductivity and contributing to the development of safer, higher-energy phosphate cathodes for next-generation LIBs.

2. Materials and Methods

Pristine and B-doped LCP (LCP-B) were synthesized using a two-step solid-state method. Stoichiometric amounts of Li_2CO_3, $NH_4H_2PO_4$, $Co(NO_3)_2 \cdot 6H_2O$, and H_3BO_3 as the boron source in the case of LCP-B, were first mixed in a planetary ball mill at 400 rpm for 10 min. Planetary ball milling was employed to ensure homogeneous mixing of precursors and uniform distribution of boron at low doping levels, which is difficult to achieve by manual grinding. After drying at 60 °C, 11 wt.% sucrose was added as a carbon source, followed by additional milling. The mixture then underwent a two-step calcination process in a tubular furnace in an argon atmosphere,

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with a temperature ramp from 350 to 550 °C at a rate of 5 °C/min for 5 h. After natural cooling, the resulting powders were ground in an agate mortar. The boron content in the doped sample was approximately 2 wt.%, corresponding to x ≈ 0.02 in $LiCo_{1-x}B_xPO_4$, defined by the precursor ratio used during synthesis. In this work, a single optimized boron-doped composition was investigated to demonstrate the feasibility and preliminary effect of boron incorporation.

3. Results and Discussion

LCP crystallizes in an orthorhombic olivine-type structure (Pnma), where Co^{2+} ions occupy CoO_6 octahedra and P^{5+} resides in PO_4 tetrahedra, forming a stable three-dimensional framework. However, its low electronic and ionic conductivity requires compositional adjustments for improved performance. XRD analysis shows that both pristine and B-doped samples retain the Pnma structure without detectable secondary phases (Fig. 1a), indicating high phase purity. The slight rightward shift of the (311) diffraction peak observed for LCP-B (Fig. 1b) is consistent with lattice distortion associated with boron incorporation, while peak broadening and intensity variations suggest changes in crystallite size and the presence of local structural defects.

The observed peak shift is consistent with lattice distortion associated with boron incorporation into the LCP structure. Such distortion is likely related to local structural perturbations induced by boron incorporation rather than ideal long-range substitution at a specific crystallographic site. Despite these distortions, the retention of the Pnma phase indicates that the overall olivine-type framework remains structurally stable. Considering the small ionic radius and preferred coordination environment of boron, its incorporation into the LCP lattice may occur via multiple mechanisms. In addition to possible defect-associated perturbations near Co sites, alternative pathways such as partial substitution of P^{5+} within PO_4 tetrahedra or defect-assisted incorporation involving interstitial boron species, accompanied by charge compensation, cannot be excluded. According to Shannon's effective ionic radii [24], Co^{2+} in octahedral coordination has a radius of ~0.745 Å, whereas B^{3+} and P^{5+} in tetrahedral coordination exhibit much smaller radii (~0.11 Å and ~0.17 Å, respectively), supporting the likelihood of local lattice distortion rather than ideal long-range substitution.

The morphology of LCP and LCP-B were investigated using SEM analysis. Pristine LCP (Fig. 2a) exhibited agglomerated, rounded particles with sizes ranging from ~200-500 nm, featuring surface voids that may hinder conductivity. At the same time, such morphology can facilitate electrolyte penetration and support lithium-ion transport. In contrast, LCP-B (Fig. 2b) shows a finer and more uniform distribution of smaller particles, with sizes in the range of approximately 100-300 nm. The reduced particle size and increased surface area provide a larger number of active sites for lithium intercalation and shorten lithium-ion diffusion pathways. In combination with the observed lattice distortion, these morphological features are expected to contribute to improved ionic and electronic transport, which is consistent with the reduced charge-transfer resistance (R_{ct}) and enhanced lithium-ion diffusion (D_{Li+}) observed in the electrochemical measurements.

In the Raman spectra Fig. 3 (a) pristine $LiCoPO_4$ exhibits the characteristic vibrational modes of the

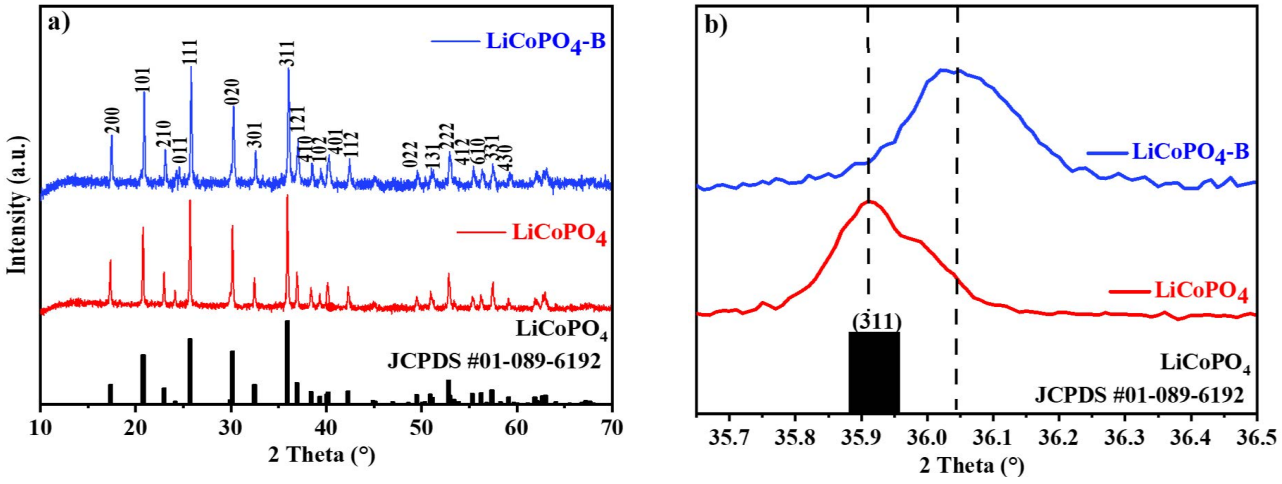

Fig. 1. XRD patterns of (a) pristine LCP and LCP-B, (b) enlarged view of the (311) plain.

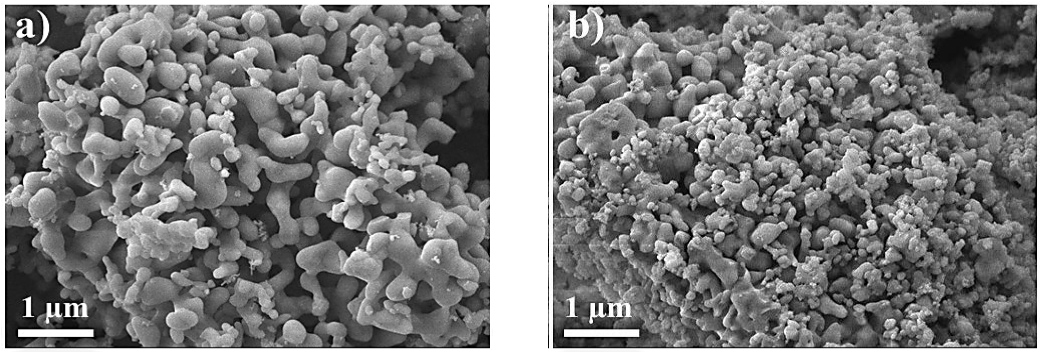

Fig. 2. SEM Images of (a) pristine LCP and (b) LCP-B synthesized via solid-state method.

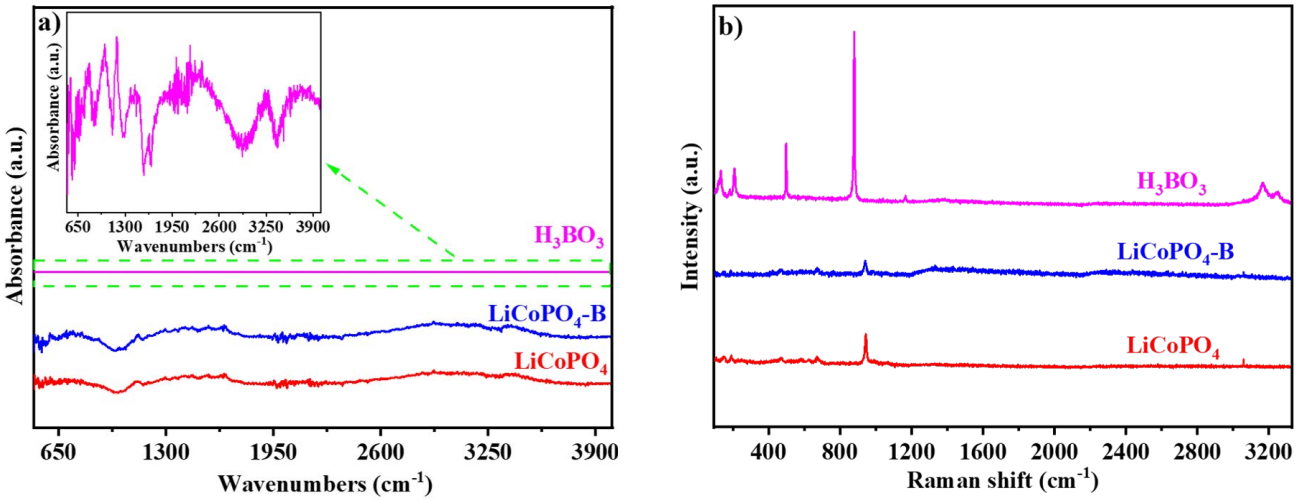

Fig. 3. Raman (a) and FTIR (b) spectra of pristine and B-doped $LiCoPO_4$ with H_3BO_3 reference.

$(PO_4)^{3-}$ tetrahedra, with strong bands centered at ~950-960 cm^{-1} (ν_1 symmetric stretching) and ~1070-1085 cm^{-1} (ν_3 antisymmetric stretching). Upon B doping these bands become lightly broadened, with small shifts on the order of a few cm^{-1} (within experimental uncertainty) toward higher wavenumbers, indicating local lattice distortions and possible shortening of P–O bonds due to charge compensation. Additional weak features appear around 700-750 cm^{-1}, which can be attributed to bending vibrations perturbed by the presence of B–O linkages. In the FTIR spectra Fig. 3 (b), both pristine and B-doped samples show the typical absorption of PO_4 groups in the regions ~1000-1100 cm^{-1} (ν_3), 930-950 cm^{-1} (ν_1), 520-600 cm^{-1} (ν_4), and 420-470 cm^{-1} (ν_2). In $LiCoPO_4$-B, slight changes in relative intensity and a shoulder near ~880-890 cm^{-1} are observed, which overlap with the expected B–O stretching vibrations. While weak due to the low B content, these modifications provide complementary evidence of boron incorporation.

The electrochemical performance of LCP-based coin cells was assessed using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) to evaluate specific capacity and cycling stability. For each composition, at least three coin cells were assembled and tested under identical conditions, showing reproducible electrochemical behavior. CV and GCD measurements were conducted at room temperature in a 3.0-5.5 V range with a scan rate of 0.1C (Fig. 4 a-b), revealed redox peaks corresponding to Co^{2+}/Co^{3+} transitions during lithium insertion and extraction.

Compared to pristine LCP, the LCP-B exhibited sharper, more symmetric peaks with reduced potential separation, indicating improved redox reversibility and better Li^+ kinetics to boron-induced lattice modifications. EIS results (Fig. 4 c-d) demonstrates a lower initial R_{ct}, slower resistance growth, and more stable ion diffusion than pristine LCP. While EIS reflects improvements in charge-transfer and interfacial resistance, the delivered capacity remains limited by electrolyte oxidation and high-voltage interfacial side reactions, which do not scale linearly with reductions in R_{ct}.

The specific capacity of the cell was determined through GCD (Fig. 5 a-d) cycling. The areal mass loading was 1.4 $mg \cdot cm^{-2}$ for LCP and 1.5 $mg \cdot cm^{-2}$ for LCP-B.

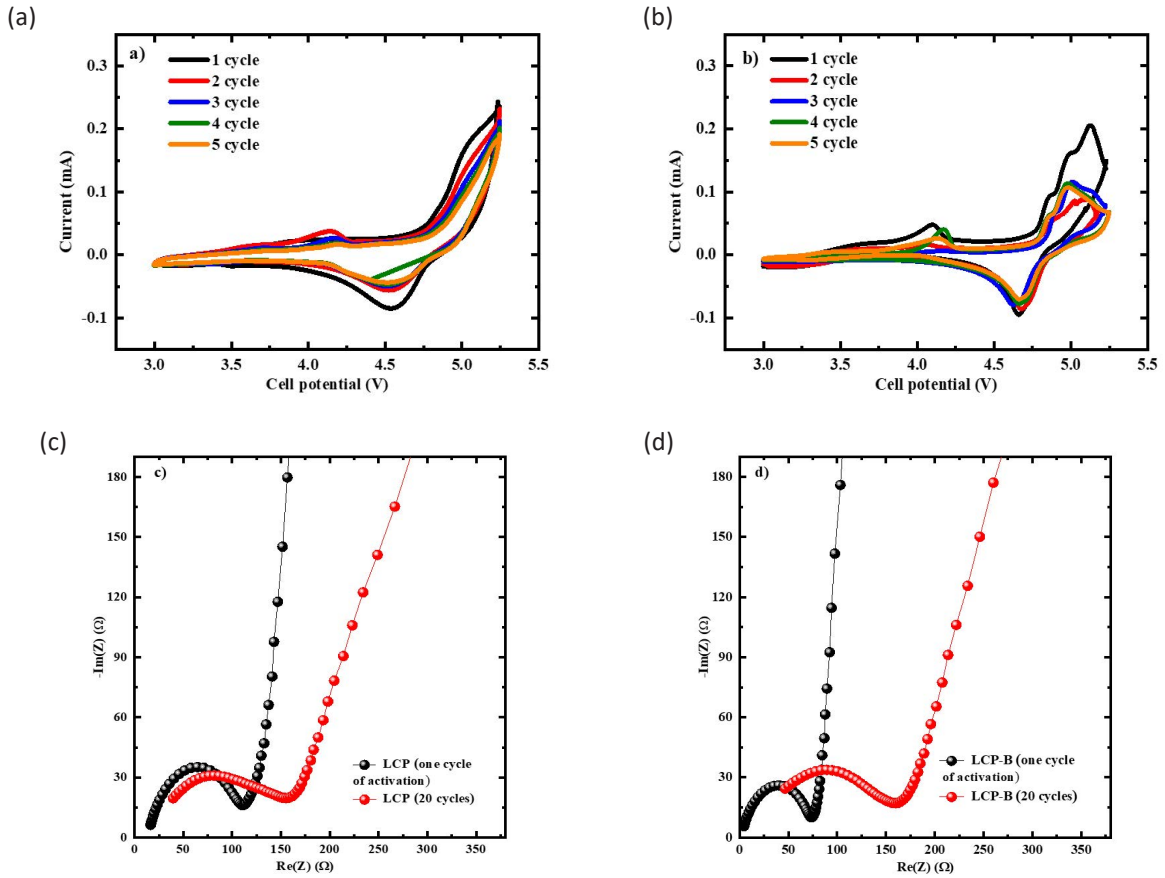

Fig. 4. Electrochemical characterization: CV curves of (a) LCP and (b) LCP-B; EIS after activation and 20 cycle for (c) LCP and (d) LCP-B.

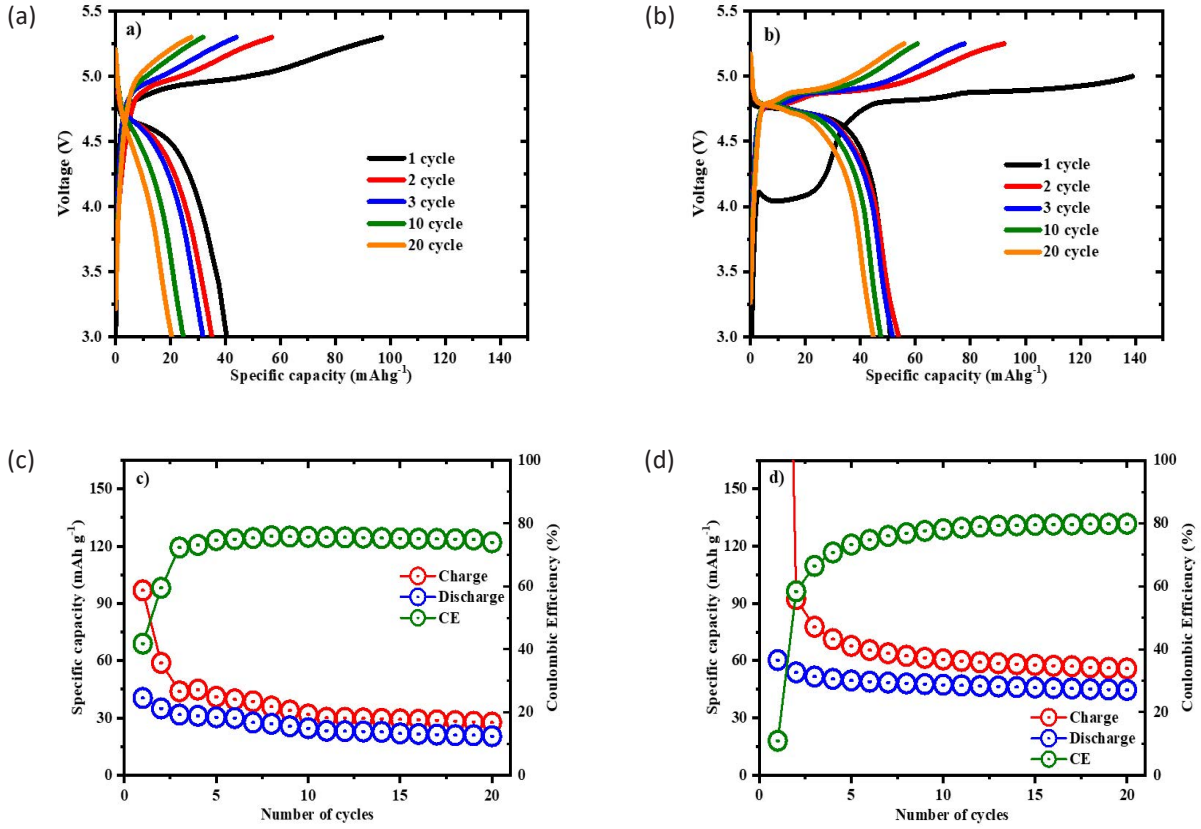

Fig. 5. GCD curves and cycling stability profiles of (a, c) pristine LCP and (b, d) B-doped LCP (LCP-B) at a 0.1C rate.

Capacity retention and coulombic efficiency were analyzed to evaluate the degradation behavior of the LCP cathode material during repeated cycles. The B-doped sample showed higher discharge capacity and improved stability over 20 cycles, with discharge capacity decreased from ~58 mAh·g^{-1} (1st cycle) to ~43 mAh·g^{-1} (20th cycle), compared to a drop from ~40 mAh·g^{-1} (1st cycle) and ~25 mAh·g^{-1} (20th cycle) in the undoped LCP. LCP-B also exhibited a more stable coulombic efficiency of ~78-81%, compared to ~70-74%. Obtained capacities are lower than some literature reports [22, 23], but demonstrate to enhance conductivity and interfacial behavior in LCP. This is consistent with the EIS data, which show a lower initial R_{ct}, slower resistance growth, and more stable ion diffusion, confirming improved conductivity and interfacial stability upon boron incorporation. The relatively low specific capacity compared to the theoretical value is attributed to the well-known kinetic limitations and interfacial instability of $LiCoPO_4$ at high cutoff voltages, as widely reported in the literature.

4. Conclusion

The optimal synthesis conditions for LCP-B were identified as 550 °C for 5 h, ensuring a well-crystallized material. Boron incorporation led to improved conductivity and interfacial stability, as evidenced by lower charge-transfer resistance and more stable cycling, with ~50% higher capacity retention after 20 cycles compared to pristine LCP. These findings demonstrate that B-doping is a promising but preliminary strategy that warrants further optimization for high-voltage phosphate cathodes.

Author contributions

Abylay Abilkhan: Writing – original draft, Writing – review & editing, Investigation. **Valeria Volobuyeva:** Data curation, Writing – original draft, Writing – review & editing. **Saparbek Tugelbay:** Validation, Visualization. **Dauren Batyrbekuly:** Supervision. **Fail Sultanov:** Supervision. **Nurzhan Umirov:** Supervision. **Batuhan Tatykayev:** Conceptualization, Methodology, Supervision.

Conflict of interest statement

The authors declare that they have no conflict of interest.

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Бор-легированный $LiCoPO_4$ как высоковольтный катод для литий-ионных аккумуляторов

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АННОТАЦИЯ

Целью данной работы является исследование влияния легирования бором на катодный материал $LiCoPO_4$ (LCP) с акцентом на проводимость и межфазные процессы. Исходный и легированный бором LCP синтезированы двухстадийным твердофазным методом. Методы рентгенофазового анализа и электронной микроскопии подтвердили фазовую чистоту, искажение кристаллической решетки и уменьшение размера частиц в легированном образце. Электрохимическая импедансная спектроскопия показала улучшение диффузии литий-ионов, повышение кулоновской эффективности (до ~75% по сравнению с ~65%) и умеренное сохранение емкости для легированного образца (~60 мА·ч·г$^{-1}$ после 20 циклов) по сравнению с исходным LCP. Полученные результаты показывают, что легирование бором эффективно повышает проводимость и снижает межфазные ограничения в LCP, представляя собой перспективную, но пока предварительную стратегию для разработки высоковольтных катодных материалов для литий-ионных аккумуляторов.

Ключевые слова: $LiCoPO_4$, легирование бором, высоковольтные катодные материалы, литий-ионные аккумуляторы

Бормен легирленген $LiCoPO_4$ литий-ионды аккумуляторларға арналған жоғары кернеулі катод

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АҢДАТПА

Бұл жұмыстың негізгі мақсаты – бор қоспасының $LiCoPO_4$ (LCP) катод материалдарының қасиеттеріне әсерін, әсіресе электрөткізгіштік пен фазалар аралық процестер тұрғысынан зерттеу. Бастапқы және бор қосылған LCP екі сатылы қатты фазалық әдіспен синтезделді. Рентгендік фазалық талдау және электрондық микроскопия нәтижелері легирленген үлгіде фазалық тазалықтың сақталғанын, кристалдық тордың бұрмалануын және бөлшек өлшемінің кішіреюін көрсетті. Электрохимиялық импеданстық спектроскопия литий иондарының диффузиясының жақсарғанын, кулондық тиімділіктің артқанын (шамамен 75%, бастапқы үлгідегі ~65% салыстырғанда) және сыйымдылықтың салыстырмалы түрде сақталуын (~60 мА·сағ·г$^{-1}$, 20 циклдан кейін) көрсетті. Бұл нәтижелер бор қоспасының LCP материалындағы электрөткізгіштікті арттырып, фазалар аралық шектеулерді азайтатынын дәлелдейді және жоғары кернеулі литий-иондық аккумулятор катодтарын дамыту үшін перспективалы, бірақ әлі де бастапқы деңгейдегі тәсіл екенін көрсетеді.

Түйін сөздер: $LiCoPO_4$, бормен легирлеу, жоғары кернеулі катод материалдары, литий-ионды аккумуляторлар