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# Development of solid-state composite cathode material for solid-state lithium-ion batteries based on lithium ferrophosphate $LiFePO_4$

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**Abstract.** In the past few decades all-solid-state lithium-ion batteries have become a promising frontier due to their increased safety, higher energy density and unique mechanical properties. One of the main issues in this field is establishing steady transport of lithium ions across the electrode–electrolyte interface, which requires modifications of the electrode structure. In this research we investigated mechanical properties, capacity and cycling performance of a composite cathode based on solid polymer electrolyte as a binder, lithium ferrophosphate as active material and carbon black as electron conductor. Composite cathode was prepared with the help of ball-milling to reduce the particle size and increase the homogeneity of the material, which resulted in mechanically stable flexible crack-free electrodes after coating, drying and calendaring. Achieved specific capacity of the electrodes corresponds to theoretical values, electrodes show long-term sustainability in systems with liquid electrolyte and are applicable to solid-state systems.

**Keywords:** All-solid-state lithium-ion battery, composite electrodes, lithium ferrophosphate electrodes, solid electrolyte, polymer electrolyte

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# Разработка твердотельного композитного катодного материала для твердотельных литий-ионных аккумуляторов на основе феррофосфата лития $LiFePO_4$

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**Аннотация.** За последние несколько десятилетий твердотельные литий-ионные аккумуляторы стали перспективным направлением науки благодаря их повышенной безопасности, более высокой плотности энергии и уникальным механическим свойствам. Одной из основных проблем в этой области является обеспечение устойчивого переноса ионов лития через границу раздела электрод-электролит, требующего модификации структуры электрода. В данной работе были исследованы механические свойства, емкость и циклические характеристики композитного катода на основе твердого полимерного электролита в качестве связующего, феррофосфата лития в качестве

активного материала и сажи в качестве электронного проводника. Композитный катод был изготовлен с помощью планетарной мельницы для уменьшения размера частиц и повышения однородности материала, в результате чего после нанесения покрытия, сушки и каландрирования получились механически устойчивые гибкие электроды без трещин. Достигнутая удельная емкость электродов соответствует теоретическим значениям, электроды демонстрируют долговременную устойчивость в системах с жидким электролитом и могут быть использованы в твердотельных системах.

**Ключевые слова:** Твердотельные литий-ионные аккумуляторы, композитные электроды, электроды с феррофосфатом лития, твердый электролит, полимерный электролит

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## Introduction

Compared to the commonly used lithium-ion batteries with liquid electrolyte, all-solid-state lithium-ion batteries offer a number of significant advantages: increased safety due to the elimination of flammable organic liquid electrolyte materials, retarding dendritic growth, allowing to use metal lithium as anode, increased mechanical stability. Stable contact between the solid electrolyte and the electrodes can be achieved, for example, by using composite electrode materials that help blur the interphase boundary, reduce its resistance and increase the maximum battery current. Unlike traditional Li-ion batteries, where liquid electrolyte infiltrates the pores of an electrode during cell assembly, the pores of composite solid-state electrodes are filled with solid polymer electrolyte at the stage of manufacturing the electrodes themselves, before assembling the cell [1]. Polymer electrolyte used instead of traditional binder ensures both mechanical integrity and ionic conductivity throughout the volume of the electrode. Uniform distribution of the active material particles, carbon and electrolyte in the electrode material results in high and uniform ionic and electronic conductivity throughout the volume of the electrode, close contact of the particles with each other and with the current collector and decreasing resistance of the electrode–electrolyte interface. A schematic representation of a battery with a composite electrode is shown in Fig. 1.

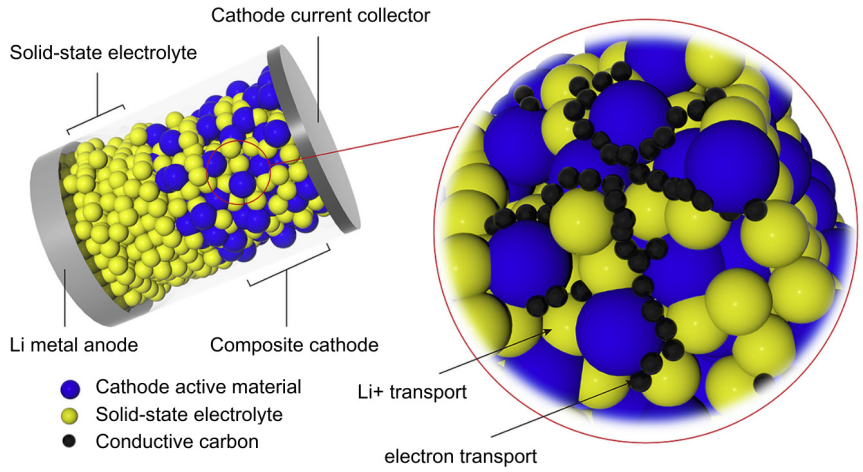


Fig. 1. Schematic of interfaces in all-solid-state Li-ion batteries [2]

Most solid polymer electrolytes for li-ion batteries are usually composed of polymer matrix and soluble lithium salt. The most common choice for polymer matrix is polyethylene oxide (PEO) since its ethylene oxide (EO) units have a higher donor number for $Li^+$ which determines relatively high ionic conductivity ($10^{-4}$ Sm/cm). The most favorable candidates for lithium source in this system are salts with large complex anions that can easily dissociate in PEO matrix and release $Li^+$ ions like LiTFSI [3], LiFSI [4] or LiBETI [5]. Principles of ion transport in PEO via interchain or intrachain hopping across the chain while forming and breaking Li-O bonds are shown in Fig. 2.

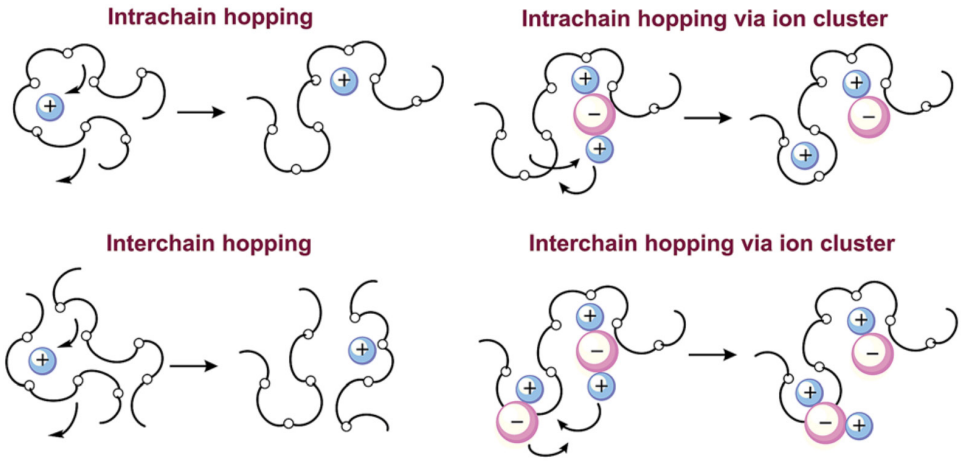


Fig. 2. Mechanism of ion transport in PEO [3]

## Materials and Methods

Two modifications of composite positive electrodes based on lithium ferrophosphate were investigated: a mixture based purely on lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and polyethylene oxide (PEO) dissolved in acetonitrile ($C_2H_3N$), further referred to as electrode A, and similar mixture based on PEO and LiTFSI with the addition of polyvinylidene fluoride (PVDF) polymer binder for mechanical stability, further referred to as electrode B. The mass ratio for PEO and LiTFSI was calculated from the optimal molar ratio EO:Li = 8:1 (1 $Li^+$ ion per 8 ethylene oxide segments) that showed the highest ionic conductivity and transference number under standard operating conditions [6].

Polymer electrolyte was mixed with the help of TWCL-B Magnetic Stirrer in argon atmosphere. The optimal cathode slurry contained 35 mass% of electrolyte binder, 5 mass% of carbon black Super P, 60 mass% of active material $LiFePO_4$ and was ball-mixed in Retsch Planetary Ball Mill Pm 100 for 2 hours at 300 rpm at room temperature, then coated on aluminum foil with TMAX-TCC1 Compact Tape Casting Coater, dried at Vacuum Drying Chamber Binder VD-115 at 50 °C for 24 hours and subjected to pressing with the help of LabTools Laboratory Hydraulic Press. Laser cutting was utilized to define the electrode topology. Standard CR2032 coin-cell batteries with $LiPF_6$ liquid electrolyte were assembled to test capacity and efficiency of the electrode material.

## Results and Discussion

By varying the composition and manufacturing conditions, high adhesion of the material to the aluminum current collector was achieved. The manufactured electrodes with mass loadings of 4.3 mg/cm$^2$ and 7.5 mg/cm$^2$ for electrode A and electrode B accordingly were examined in half-cells with lithium metal anode and liquid electrolyte. Capacity measurements were performed with the help of Neware Battery Testing System at 0.1C current rate. During the first five cycles the average specific capacity of mixture A reached and preserved a value of 149 mA·h/g with Coulomb efficiency of 97.8% whereas specific capacity of mixture B reached and preserved a value of 165 mA·h/g with Coulomb efficiency of 98.9%, which corresponded to theoretical

value of 165 mAh/g for LFP. Higher specific capacity and capacity retention of the latter during cycling proves the usage of additional polymer binder (in this case PVDF) to be beneficial for battery performance, despite possible increase in interphase resistance due to its poor conducting qualities. It is suggested that the presence of PVDF helped improve mechanical stability of the electrode and prevent microcracks formation during active material particles volume expansion within charge-discharge process.

Due to its promising specifications electrode B was also examined in coin-cell against similar anode based on PEO, PVDF, LiTFSI and S-360 graphite as active material. Specific capacity of resulting battery kept growing and reached 130 mA·h/g during the first five cycles; Coulomb efficiency increased from 95.5% to 98.5% as well. Charge-discharge curves for electrode A against metal Li, electrode B against metal Li and electrode B against graphite anode are present at Fig. 3.

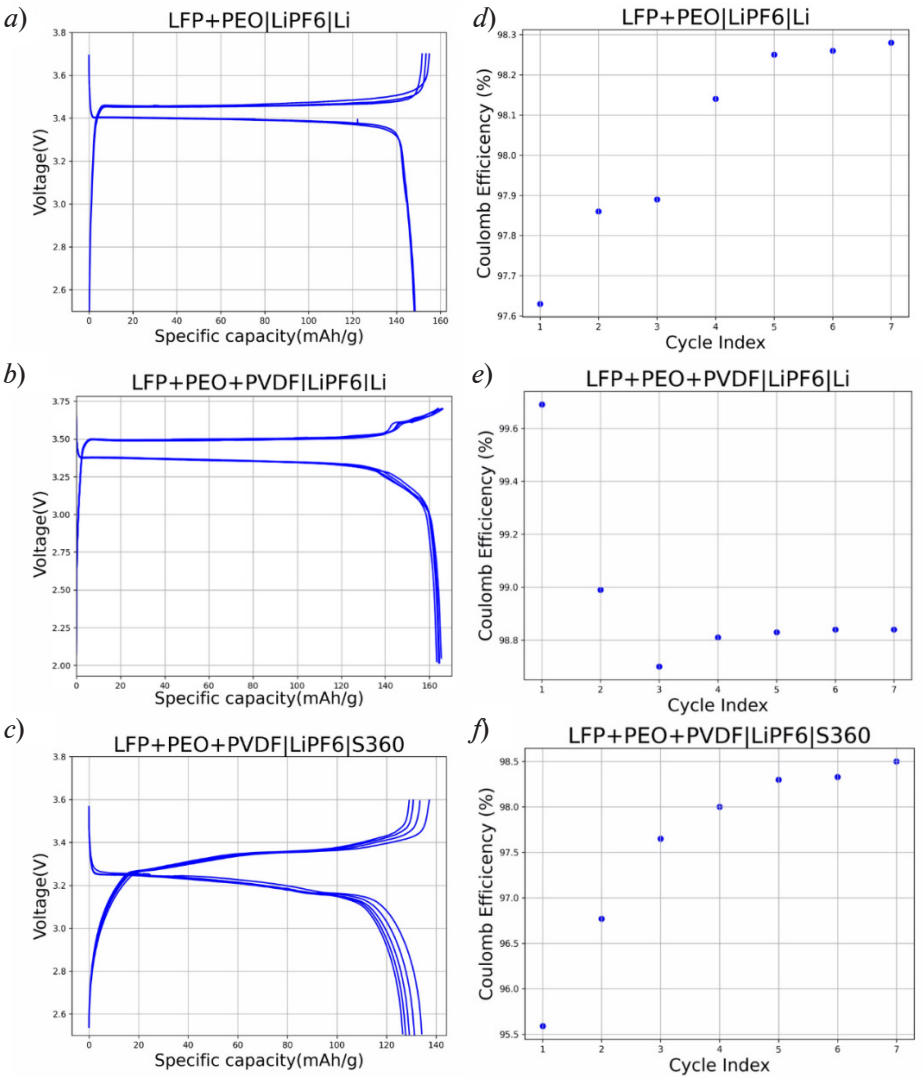


Fig. 3. Charge-discharge curves (*a*, *b*, *c*) and cycling performance (*d*, *e*, *f*) of electrode A and electrode B half-cells and electrode B full cell against graphite

## Conclusion

Investigated polymer-based lithium ferrophosphate cathode material shows promising mechanical characteristics and specific capacity. It is applicable for batteries with PEO-based solid electrolytes, a popular subject of scientific research in the field of all-solid-state batteries. Electrochemical testing of LFP electrodes was carried out using coin-cells with lithium metal and

graphite negative electrodes. Electrodes with additional binder, PVDF, showed higher mechanical properties, increase in specific capacity (148.8 vs 165.4 mA·h/g) and Coulomb efficiency (97.8% vs 98.9% compared to those without due to higher mechanical stability and microcracks formation tolerance. Investigated material has the potential to be utilized in all-solid-state batteries Further research on composite electrode materials for all-solid-state Li-ion batteries is vital for development of safe, sustainable and mobile energy sources.

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