Electrolytes in the \([\text{N}_{13}\text{pip}]\text{ClO}_4-\text{LiClO}_4-\text{Al}_2\text{O}_3\) system for solid state lithium batteries

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Abstract

The transport, electrochemical, structural, and thermal properties of electrolytes in the ternary system \([\text{N}_{13}\text{pip}]\text{ClO}_4-\text{LiClO}_4-\gamma\text{-Al}_2\text{O}_3\) (\(\text{N}_{13}\text{pip}\) is \(N\)-methyl-\(N\)-ethyl-piperidinium cation) were investigated at the molar ratio \([\text{N}_{13}\text{pip}]\text{ClO}_4: \text{LiClO}_4 = 0.82:0.18\). The addition of alumina leads to a change in the thermodynamic properties of the \([\text{N}_{13}\text{pip}]\text{ClO}_4-\text{LiClO}_4\) system that can be explained by a partial transfer of lithium perchlorate from the organic phase to the surface of \(\gamma\text{-Al}_2\text{O}_3\). The highest ionic conductivity of 6.2\(\times\)10\(^{-4}\) S/cm at 110 °C was observed for the composition containing the volume fraction (\(f\)) of \(\gamma\text{-Al}_2\text{O}_3\) equal to 0.5. The increase in conductivity compared to the binary system \(0.82[\text{N}_{13}\text{pip}]\text{ClO}_4-0.18\text{LiClO}_4\) is achieved due to the amorphization of the organic salt near the salt/LiClO\(_4\)/oxide interfaces. Galvanostatic cycling with Li electrodes shows that composites with \(f = 0.5\) are stable at 110 °C for at least 68 charge/discharge cycles, and the electrolyte is shown to be electrochemically stable up to 5 V. This system can be used as a solid-state electrolyte in lithium-ion current sources.

Key findings

• The transport, electrochemical, structural, and thermal properties of electrolytes in the ternary system \([\text{N}_{13}\text{pip}]\text{ClO}_4-\text{LiClO}_4-\gamma\text{-Al}_2\text{O}_3\) were investigated.

Keywords

solid state ionics
organic ionic plastic crystals
lithium-ion current sources
solid composite electrolytes
ionic conductivity

1. Introduction

Currently, lithium-ion current sources with liquid electrolytes are widespread. However, they have several disadvantages. Standard liquid electrolytes based on carbonates promote the lithium dendrite formation [1]. During the charge and discharge processes, non-uniform deposition of lithium occurs with the formation of needle-like structures – dendrites. Eventually, the dendrites can penetrate the separator and reach the cathode, causing a short circuit.

The second problem is related to the use of volatile solvents as a component of the liquid electrolyte. Due to the high saturated vapor pressure of these substances, there is a possibility of explosion and ignition of the device. In addition, due to mechanical instability, there is a risk of electrolyte leakage. Another problem of chemical power sources with liquid electrolytes is the need for a separator to prevent short circuits. All of the above problems can be solved by replacing liquid electrolytes with solid electrolytes.

Organic ionic plastic crystals (OIPCs) have been recently used as solid electrolytes [2, 3]. Plastic crystals have a solid-solid phase transition to the structurally disordered phases, which can promote ion transport [4, 5]. OIPCs have good electrochemical stability [6], low saturated vapor pressure, high thermal stability [7], small entropy of mixing [8], and a relatively high ionic conductivity [9], which is achieved due to the rotational movement of organic groups [10, 11]. OIPCs based on imidazolium...
N-methyl-N-propylpyrrolidinium perchlorate was synthesized in two steps. Firstly, 0.0827 mol of N-methyl piperidinium, 0.1655 mol of n-propyl bromide, and 30 mL of acetonitrile were placed in a round bottom flask equipped with a magnetic stirrer and a reflux condenser. Then the mixture was boiled under stirring until the neutral reaction of wet indicator paper. As a result, N-methyl-N-propylpyrrolidinium bromide, \([\text{N}_3\text{pip}]\text{Br}\), was prepared according to the reaction:

\[
\text{CH}_3\text{NC}_5\text{H}_10 + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \\
\rightarrow [(\text{CH}_3)(\text{CH}_3\text{CH}_2\text{CH}_2)\text{NC}_5\text{H}_10]\text{Br} \quad (1)
\]

The precipitate of \([\text{N}_3\text{pip}]\text{Br}\) was filtered off, washed with diethyl ether, and dried. In the second stage, a solution of 0.06736 mol \([\text{N}_3\text{pip}]\text{Br}\) in 20 mL water was added to 0.03368 M aqueous solution of lead perchlorate with the formation of a water solution of N-methyl-N-propylpyrrolidinium \([\text{N}_3\text{pip}]\text{ClO}_4\) by the reaction:

\[
2[(\text{CH}_3)(\text{CH}_3\text{CH}_2\text{CH}_2)\text{NC}_5\text{H}_10]\text{Br} + \text{PbClO}_4 \rightarrow 2[(\text{CH}_3)(\text{CH}_3\text{CH}_2\text{CH}_2)\text{NC}_5\text{H}_10]\text{ClO}_4 + \text{PbBr}_2 \quad (2)
\]

The obtained solution was separated was PbBr\(_2\) by filtration and evaporated. For removal of traces of lead chloride, the precipitate was dissolved in acetonitrile, the remaining precipitate was filtered, and then the solution was evaporated again. The obtained product was finally recrystallized from a mixture of ethyl acetate and ethyl alcohol.

Lithium perchlorate was synthesized by the reaction between perchloric acid HClO\(_4\) and lithium carbonate Li\(_2\)CO\(_3\) according to the reaction:

\[
2\text{HClO}_4 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiClO}_4 + \text{H}_2\text{O} + \text{CO}_2 \quad (3)
\]

Aluminum oxide γ-Al\(_2\)O\(_3\) (surface area 200 m\(^2\)/g, specification IKT-02-6M; JSC Katalizator, Novosibirsk, Russia) was preheated in a muffle furnace at 600 °C for 2 h for dehydration.

To obtain the composites, \([\text{N}_3\text{pip}]\text{ClO}_4\) was mixed with LiClO\(_4\) in a molar ratio of 0.82:0.18 with the addition of ethyl alcohol. The obtained mixture was dried in air and then in a vacuum oven at 170 °C for 12 h. The obtained binary system was mixed in with γ-Al\(_2\)O\(_3\) in different ratios in the concentration range of 30–80 vol.% of γ-Al\(_2\)O\(_3\). Further in the text, the parameter \(f\) will indicate the volume fraction of aluminum oxide.

### 2.2. Methods

The thermal properties of composites were investigated by differential scanning calorimetry using a DSC500 device. The samples were placed in aluminum pans and heated at a rate of 10 °C/min. The analysis was performed in an argon atmosphere at a flow rate of 0.05 L/min. The data recorded at the second heating are
presented in the paper. The structural properties were studied by X-ray diffraction on a BRUKER D8 ADVANCE diffractometer. For conductivity measurements, of the composites were compacted at 400 bar to pellets 0.5 cm in diameter with silver electrodes. The measurements were carried out at AC voltage in the frequency range of 30 Hz - 1 MHz by HP-4284A Hewlett Packard Precision LCR Meter in a vacuum of 5·10^{-2} Torr in a stepwise temperature change mode in the range of 25-150 °C. Electrochemical studies were carried out on CR2032-type cells assembled in a glove box in an argon atmosphere. Electrochemical stability in contact with metallic lithium was investigated by galvanostatic cycling of symmetric cells with lithium electrodes at a current density of 0.05 mA/cm² and a temperature of 110°C. Impedance data were obtained after cycling using the Electrochemical station Zive SP2. The electrochemical window was determined by linear voltammetry using a SmartStat PS-50 instrument at \( T = 110 \) °C. Stainless steel was used as the working electrode, and lithium metal was used as the reference electrode. The rate of potential sweep was 1 mV/s.

3. Results and Discussion

3.1. Thermal properties

During the first heating of the initial three-phase mixture from 25 to 190 °C, the interaction between the components takes place, accompanied by several peaks due to phase transitions in the organic salt and dehydration of the components. Therefore, for further analysis, only data obtained during the second heating were used. Figure 1 shows the as-obtained DSC curves in the temperature range of 30-190 °C.

A pure organic salt \([\text{N}_{13}\text{pip}]\text{ClO}_4\) has two overlapping thermal effects at 117 °C and 125 °C. The first peak refers to the transition to the high-temperature disordered phase characteristic of this class of compounds, and the second peak refers to melting. Two thermal effects are also observed for \([\text{N}_{13}\text{pip}]\text{ClO}_4\) containing 0.18 mole fraction of lithium perchlorate at \( T \approx 60 \) °C and \( T \approx 105 \) °C. The first thermal effect is due to the polymorphic phase transition, while the second one is due to melting. The decrease in melting temperature is due to the formation of a eutectic mixture with the composition 0.82\([\text{N}_{13}\text{pip}]\text{ClO}_4\)-0.18LiClO₄. After doping with heterogeneous additive γ-Al₂O₃ in an amount of 30 vol.%, two thermal effects are observed at temperatures corresponding to the temperatures of thermal effects of pure organic salt. A possible reason for the observed effect is the high adhesion of lithium perchlorate to the surface of the oxide additive. As a result, the salt is practically completely transferred to the surface of the γ-Al₂O₃ particles, leading to the disintegration of the eutectic mixture to the mixture of pure \([\text{N}_{13}\text{pip}]\text{ClO}_4\) in which \(\text{LiClO}_4/\text{Al}_2\text{O}_3 \) particles are embedded. At higher concentrations of the γ-Al₂O₃, the intensity of the thermal effects of the ionic salt decreases, and at the volume fraction of γ-Al₂O₃ \( f \geq 0.5 \), the thermal effects due to phase transition and melting of the salt vanish. The most possible reason for this is the transition of the salt to the amorphous state. This effect is typical for ionic salt-oxide systems and was previously observed in the systems LiClO₄-A (A = MgO [31], Al₂O₃ [32]), (n-Bu)₄NBF₄-Al₂O₃ [33], [(CH₃)(n-C₃H₆)NC₃H₇H]BF₄-X (X = SiO₂, Al₂O₃) [22], (n-C₄H₉)NBF₄-Y (Y=MgO, Al₂O₃) [34, 35], N-ethyl-N-methyl pyrrolidinium bis(trifluoromethane sulfonyl)amide (C₅H₅pyr[TFSI]) – Z (Z = TiO₂, SiO₂) [36]. It was also observed in OIPC-polymer composite systems by NMR [37, 38].

3.2. Structural properties

Figure 2 shows the data of X-ray phase analysis of both initial compounds (\([\text{N}_{13}\text{pip}]\text{ClO}_4\), LiClO₄), the binary system 0.82\([\text{N}_{13}\text{pip}]\text{ClO}_4\)-0.18LiClO₄ before and after doping with aluminum oxide.

![Figure 1: The DSC curves for some [0.82\text{N}_{13}\text{pip}]\text{ClO}_4\]-0.18\text{LiClO}_4-\text{Al}_2\text{O}_3 composites.](image)

![Figure 2: The diffraction patterns of pure \text{LiClO}_4 (1), pure \([\text{N}_{13}\text{pip}]\text{ClO}_4\) (2), initial mixture 0.82\([\text{N}_{13}\text{pip}]\text{ClO}_4\)-0.18\text{LiClO}_4 (3) and composites 0.82\([\text{N}_{13}\text{pip}]\text{ClO}_4\)-0.18\text{LiClO}_4-Al₂O₃ containing 30, 40, 50 and 60 vol.% alumina, curves (4), (5), (6) and (7), respectively.](image)
It can be seen that in the binary system, there are reflections of pure N-methyl-N-propylpiperidinium perchlorate and reflections that do not correspond to any of the initial components of the mixture. These reflections may be related to a new phase of double salt. To identify a new phase, the phase diagram of the binary system \([\text{[N}_3\text{pip}]\text{ClO}_4-\text{LiClO}_4\) should be investigated. Such work is in progress now. The introduction of \(\gamma\text{-Al}_2\text{O}_3\) heterogeneous additive results in two effects (see curves (4)–(7) in Figure 2): (i) only the reflections corresponding to pure \([\text{[N}_3\text{pip}]\text{ClO}_4\) are present in the X-ray patterns of \(0.82[\text{[N}_3\text{pip}]\text{ClO}_4-0.18\text{LiClO}_4-\text{Al}_2\text{O}_3\) composites. The observed effect correlates well with the results of differential scanning calorimetry and confirms the assumption that lithium perchlorate is adsorbed on the surface of aluminum oxide as an amorphous layer which gives no X-ray diffraction peaks; (ii) a marked decrease in the intensity of the reflections with increasing concentration of the heterogeneous dopant is observed. At the concentration of \(\gamma\text{-Al}_2\text{O}_3 ≥ 60\text{ vol.} %\), these reflections completely disappear. This effect also correlates with the data of thermal analysis, which confirms the assumption of partial or complete amorphization of N-methyl-N-propylpiperidinium perchlorate in the composites.

3.3. Transport properties

The dependence of specific conductivity on temperature is presented in Figure 3 in Arrhenius coordinates. Conductivity parameters are listed in Table 1. The conductivity values are reproduced in heating-cooling cycles, which indicates that the conductivity is not associated with metastable defects and is not due to protons of water adsorbed on the composite surface. The values of specific conductivity of the electrolyte \(0.82[\text{[N}_3\text{pip}]\text{ClO}_4-0.18\text{LiClO}_4\) abruptly change due to melting from nearly \(10^{-7}\text{ S/cm}\) to \(10^{-3}\text{ S/cm}\) (Table 1).

The addition of the heterogeneous additive leads to an increase in conductivity at temperatures below the melting point. At low concentrations of \(0.1 ≤ f ≤ 0.4\) as well as for the pure \(0.82[\text{[N}_3\text{pip}]\text{ClO}_4-0.18\text{LiClO}_4\) electrolyte, sharply increasing conductivity associated with melting is observed due to residual quantity of free salt or eutectics in the composites. At concentrations \(0.5 ≤ f ≤ 0.8\), no jump change in conductivity is observed. Moreover, at a concentration of \(f = 0.3\), the temperature dependence of conductivity is not linear in Arrhenius coordinates. The observed effect may be related to the fact that at \(f ≤ 0.5\) the conductivity curves can be described by Arrhenius dependences over the whole temperature region.

![Figure 3](image3) The temperature dependence of conductivity for composites (The third heating).

![Figure 4](image4) The dependence of composites conductivity on the volume fraction of \(\text{Al}_2\text{O}_3\).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Ionic conductivity parameters of ((1-f){0.18[\text{[N}_3\text{pip}]\text{ClO}_4-0.82\text{LiClO}_4}-f\text{Al}_2\text{O}_3) composites, where (f) is the volume fraction of alumina.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f)</td>
<td>(\sigma_{100}) ((\text{S/cm}))</td>
</tr>
<tr>
<td>0</td>
<td>(5.8\times10^{-9})</td>
</tr>
<tr>
<td>0.1</td>
<td>(8.3\times10^{-4})</td>
</tr>
<tr>
<td>0.2</td>
<td>(7.4\times10^{-4})</td>
</tr>
<tr>
<td>0.3</td>
<td>(2.5\times10^{-5})</td>
</tr>
<tr>
<td>0.4</td>
<td>(5.2\times10^{-5})</td>
</tr>
<tr>
<td>0.5</td>
<td>(1.1\times10^{-4})</td>
</tr>
<tr>
<td>0.6</td>
<td>(1.2\times10^{-4})</td>
</tr>
<tr>
<td>0.7</td>
<td>(1.2\times10^{-6})</td>
</tr>
<tr>
<td>0.8</td>
<td>(4.1\times10^{-8})</td>
</tr>
</tbody>
</table>

\(^a\)below melting temperature;  
\(^b\)above melting temperature;  
\(^c\)curve is non-linear in Arrhenius coordinates and can be described by Vogel-Fulcher-Tamman (VFT) equation.
The thermal, structural, and conductivity data can be interpreted in terms of the qualitative scheme presented in Figure 5. The overall concentration range can be separated into four regions:

- at low concentration of the alumina below the first percolation threshold all oxide particles are covered with the LiClO₄ layer, which in turn is covered by a layer of the amorphous phase of [N₁₃pip]ClO₄ located near the LiClO₄/[N₁₃pip]ClO₄ interfaces. As lithium perchlorate partially transfers from the initial composite to the alumina surface, the remaining volume of the composite is depleted in LiClO₄;

- as the concentration of alumina rises, the volume fraction of the amorphous phase increases; at f ~ 0.5 this phase occupies a total volume of [N₁₃pip]ClO₄ in the composites, and the conductivity reaches a maximum. The conductivity of the amorphous phase has non-Arrhenius behavior and can be described by the Vogel-Fulcher-Tamman equation, which is typical of amorphous compounds [39–41];

- further increase in the oxide additive content leads to a decrease in the concentration of the amorphous phase of [N₁₃pip]ClO₄, and at sufficiently high concentration of oxide, in the vicinity of the second percolation threshold, ionic transport occurs along the LiClO₄/Al₂O₃ interfaces.

- the conductivity is due to [N₁₃pip]ClO₄, which is in the amorphous state. Interestingly, at f > 0.5, s(T) dependencies follow Arrhenius dependences over the whole temperature region.

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- at low concentration of the alumina below the first percolation threshold all oxide particles are covered with the LiClO₄ layer, which in turn is covered by a layer of the amorphous phase of [N₁₃pip]ClO₄ located near the LiClO₄/[N₁₃pip]ClO₄ interfaces. As lithium perchlorate partially transfers from the initial composite to the alumina surface, the remaining volume of the composite is depleted in LiClO₄;

- as the concentration of alumina rises, the volume fraction of the amorphous phase increases; at f ~ 0.5 this phase occupies a total volume of [N₁₃pip]ClO₄ in the composites, and the conductivity reaches a maximum. The conductivity of the amorphous phase has non-Arrhenius behavior and can be described by the Vogel-Fulcher-Tamman equation, which is typical of amorphous compounds [39–41];

- further increase in the oxide additive content leads to a decrease in the concentration of the amorphous phase of [N₁₃pip]ClO₄, and at sufficiently high concentration of oxide, in the vicinity of the second percolation threshold, ionic transport occurs along the LiClO₄/Al₂O₃ interfaces. As shown earlier [32] nanocomposites LiClO₄/Al₂O₃ have a high ionic conductivity. Despite this, in the composites under study the concentration of LiClO₄ is not sufficiently high, the conductivity can be measured up to f = 0.8;

- at very high alumina concentrations above the second percolation threshold the conductive regions are separated, all conductivity pathways are broken, and the composites are insulators.

Table 2 shows the conductivity of some composite electrolytes found in the literature. It can be said that the transport properties of our system are comparable to those of other composite electrolytes.

![Figure 5 Schematic representation of composite morphology and conductivity isotherm as a function of oxide additive concentration.](image_url)
3.4. Galvanostatic test

Galvanostatic tests were performed for samples containing 40 and 50 vol.% aluminum oxide. Cycling was carried out at 110 °C in a symmetrical cell with lithium electrodes. The test sample was a disk of 2 cm² area with a thickness of 1 mm. The current density was 0.05 mA/cm². The results of galvanostatic cycling of the sample containing 50 vol.% Al₂O₃ are shown in Figure 6. It can be seen that the curves are symmetrical, indicating that the electrodes are identical. During the cycling, the voltage values were in the range of 1.5–1.6 V. At the same time, a slight increase in the potential during cycling was observed. The reason for this is most likely the formation of the SEI layer at the electrode/electrolyte interface.

The impedance hodograph of the cell and the equivalent circuit after galvanostatic tests are shown in Figure 7. The equivalent circuit includes 3 impedances connected in series: Z₁ – composite electrolyte resistance, Z₂ – charge transfer resistance and the electrode impedance represented by the constant phase element CPE₃.

\[
Z_1 = \frac{1}{R_1 + Y_1^3(i\omega)^{n_1}} \quad (4)
\]

\[
Z_2 = \frac{1}{R_2 + Y_2^3(i\omega)^{n_2}} \quad (5)
\]

\[
\text{CPE}_3 = Y_3^3(i\omega)^{n_3} \quad (6)
\]

The impedances (1) and (2) include the active resistances, R₁ and R₂, connected in parallel to the constant phase elements CPE₁ and CPE₂, respectively. Each CPE is defined by the terms Y₁, Y₂, and Y₃ the exponents n₁, n₂, and n₃, respectively. The fitting of the theoretical dependence to the experimental data was carried out using the ZView program. The fitting curve is shown in Figure 7, and the parameters of the equivalent circuit are listed in Table 3.

Figure 8 shows the results of galvanostatic tests of a symmetric cell with a sample containing 40 vol.% Al₂O₃. The cycling was carried out at 110 °C in a symmetrical cell with lithium electrodes. The sample tested was a disk of 2 cm² area with a thickness of ~0.3 mm.

The current density was 0.05 mA/cm². It can be seen that qualitatively the results of cycling of this sample are similar to the results of galvanostatic tests of composite containing 50 vol% Al₂O₃. The results of galvanostatic cycling indicate that the samples under study have an appreciable contribution to lithium-ion conductivity.

<table>
<thead>
<tr>
<th>Table 2 Conductivity of some composite electrolytes.</th>
<th>Conductivity at 40 °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO₄-Al₂O₃</td>
<td>~2·10⁻³</td>
<td>[42]</td>
</tr>
<tr>
<td>LLZTO/PVDF-HFP</td>
<td>~3·10⁻³</td>
<td>[43]</td>
</tr>
<tr>
<td>PAN-TiO₂-LiClO₄</td>
<td>~6·10⁻⁶</td>
<td>[44]</td>
</tr>
<tr>
<td>[Cmpyr][TFSI]-LiTFSI-polymer nanoparticles</td>
<td>~1·10⁻⁷</td>
<td>[27]</td>
</tr>
<tr>
<td>LiClO₄-Al₂O₃</td>
<td>~2·10⁻³</td>
<td>[32]</td>
</tr>
<tr>
<td>[N₂pip]ClO₄-LiClO₄-Al₂O₃</td>
<td>~4·10⁻⁶</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 6 Galvanostatic cycling curve obtained for the cell Li/[0.82N₂pip]ClO₄-0.18LiClO₄-Al₂O₃/Li with the electrolyte containing f(Al₂O₃) = 0.5.

Figure 7 Nyquist curve obtained at 110 °C after galvanostatic cycling test for cell Li/[0.82N₂pip]ClO₄-0.18LiClO₄-Al₂O₃/Li containing f(Al₂O₃) = 0.5.

Figure 8 The galvanostatic cycling for 68 h for Li/[0.82N₂pip]ClO₄-0.18LiClO₄-Al₂O₃/Li cell with volume fraction of Al₂O₃ f = 0.4.
3. Electrochemical stability

The electrochemical stability window of the composite concerning lithium was determined using the linear amperometry method in the voltage range of 0–5.5 V at a potential sweep rate of 1 mV/s in a cell where stainless steel (SS) was used as the working electrode (cathode) and lithium metal SS/[0.82N_{pip}]ClO_4-LiClO_4-Al_2O_3/Li was used as the reference electrode (anode). As a test sample, a composite containing 50 vol% was taken. The obtained curve is shown in Figure 9. It can be seen that there is an increase in current up to 2 V after which the current value is near zero up to a voltage of ~3.7 V. From 3.7 V and up to ~4.4 V, an increase in current by ~2.5 mA is observed. Further, the current value does not change until ~4.8 V, after which the current starts to increase. A possible reason for such behavior is the formation of a passivation layer on the surface of the steel electrode in the voltage range of 3.7–4.4 V, which prevents further electrochemical decomposition up to 4.8 V. Thus, it can be concluded that this composite electrolyte remains stable up to 5 V.

4. Limitations

The mechanism of ion conduction in OIPC has not been fully understood at this time. There is ongoing debate in the literature about this topic. In this work, we propose a possible mechanism for ionic conductivity in a composite material based on OIPC. However, further research is needed to confirm this hypothesis. For example, techniques such as infrared (IR), nuclear magnetic resonance (NMR), and Raman spectroscopy could provide valuable insights into the physical and chemical processes that occur in composites.

5. Conclusions

The composites 0.82[N_{pip}]ClO_4-0.18LiClO_4-Al_2O_3 obtained from eutectic mixture of the organic salt [N_{pip}]ClO_4 and lithium perchlorate with the nanocrystalline additive of γ-alumina with the specific surface area of 200 m^2/g were synthesized, and their thermal, structural, transport and electrochemical properties were investigated. It was found that when a heterogeneous additive of aluminum oxide is added, the amorphization of the organic salt [N_{pip}]ClO_4 takes place, and at the alumina volume fraction of f = 0.5 the salt completely transforms to the amorphous state.

At the same time, lithium perchlorate partially transfers from the bulk of the initial composite to the oxide surface. As a result, the composite becomes depleted in LiClO_4 as evidenced by the thermal analysis data. The conductivity of the composites increases with the alumina volume fraction. The maximum conductivity is achieved at the volume fraction of γ-Al_2O_3 f = 0.4–0.5. At such a concentration of the oxide, the conductivity exhibits non-Arrhenius behavior typical for amorphous conductors. According to galvanostatic cycling data, lithium ions give an appreciable contribution to the overall conductivity of the composites, and they can be used as solid electrolytes in lithium-ion batteries.

- Supplementary materials
  No supplementary materials are available.

- Conflict of interest
  The authors declare no conflict of interest.

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  None.

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**Table 3** Equivalent circuit parameters obtained for the sample before and after galvanostatic cycling.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before cycling</th>
<th>After cycling</th>
</tr>
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<tbody>
<tr>
<td>R_1</td>
<td>166±40</td>
<td>189±0.9</td>
</tr>
<tr>
<td>R_2</td>
<td>910±45</td>
<td>661±1</td>
</tr>
<tr>
<td>Y_1^p</td>
<td>(2.7±0.7)×10^{-7}</td>
<td>(1.1±0.1)×10^{-6}</td>
</tr>
<tr>
<td>n_1</td>
<td>0.73±0.05</td>
<td>0.61±0.01</td>
</tr>
<tr>
<td>Y_1^p</td>
<td>(4.2±0.4)×10^{-7}</td>
<td>(6.0±0.8)×10^{-8}</td>
</tr>
<tr>
<td>n_2</td>
<td>0.40±0.006</td>
<td>0.627±0.009</td>
</tr>
<tr>
<td>Y_1^p</td>
<td>(2.3±0.1)×10^{-4}</td>
<td>(4.1±0.05)×10^{-3}</td>
</tr>
<tr>
<td>n_3</td>
<td>0.64±0.01</td>
<td>0.407±0.007</td>
</tr>
</tbody>
</table>

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**Figure 9** Linear voltammetry curve of Li/[0.82N_{pip}]ClO_4-0.18LiClO_4-Al_2O_3/SS cell with volume fraction of Al_2O_3 f = 0.5.
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**Author contributions**

Conceptualization: N.U.

Data curation: D.K., A.U.

Formal Analysis: D.K., A.U.

Funding acquisition: Y.Y.Y., Z.Z.Z.

Investigation: D.K., A.U.

Methodology: A.U., N.U.

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**References**


