Development and study of solid-polymer electrolytes for lithium batteries

V.P. Chebotarev*, V.A. Zhorin**, S.E. Smirnov, I.A. Putsylov and S.S. Smirnov

* NIIPM; ** The N.N.Semenov Institute of Chemical Physics of the Russian Academy of Sciences; Moscow Power Engineering Institute (Technical University)

INTRODUCTION

The results obtained so far using polymers in lithium batteries show that the highest conductivity of solid-polymer electrolytes (SPEs) was achieved using amorphous polymers (Ref. 1). This is connected with the fact that it is practically impossible to introduce any additions into the crystalline phase of amorphous-crystalline polymers. Any extraneous substances introduced into the polymers are distributed in the amorphous phase. Another very important question relates to the dimensions of the heterophases that form in the amorphous phase of polymers when active components are introduced into a polymer. This is directly linked to the question of the mobility of charge carriers in polymer electrolytes. It was found that the electrical conductivity of the electrolyte increases as the glass transition temperature of the polymer decreases. This means that the segmental mobility of the polymer matrix has a substantial influence on the charge transfer process in a polyelectrolyte (Ref. 2). Thus, one of the basic requirements of a polymer matrix is high mobility at various structural levels.

Currently one of the main problems is decrease in dimensions of the crystalline phase of the polymer. The commonest methods are:

• introduction of flexible blocks into the polymer,
• introduction of elastomers into the matrix,
• structurisation of PEO,
• addition of plasticisers,
• synthesis of new organometallic salts with low lattice energy and plasticiser properties (Ref. 3).

Translation submitted by J.E. Baker

Introduction of flexible blocks is the least effective, because in this case complex formation leads to precipitation of salts. The best results were obtained using composites. Thus, SPEs with conductivity of $10^{-4}$-$10^{-5}$ $\Omega^{-1}\text{cm}^{-1}$ at room temperature were obtained with polypropylene oxide–polymethyl methacrylate (30 vol.%) composite, whereas addition of polyacrylonitrile-butadiene and polystyrene-butadiene copolymers to SPEs increases the electrical conductivity but also leads to a sharp drop in mechanical properties of the film (Ref. 4).

Structurisation of the polymers forming the basis of the SPEs is more promising. Examples are the copolymers polyethylene oxide triol and polyethylene oxide diisocyanate, polypropylene oxide and phenylisocyanate; PEO, radiation-structurised with acrylate oligomers. However, production of these networks is quite complex, but their electrical conductivity does not exceed $10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$ (Ref. 5).

Owing to the relatively low electrical conductivity of these SPEs, acceptable electrical parameters of a lithium battery (LB) can only be obtained at high temperatures (373 K and above). A long service life (1000 cycles or more) has been achieved with these LBs. In the majority of devices, however, KhIT operate at temperatures of 253 K – 343 K (Refs. 6, 7).

Mechanical methods – grinding in ball mills, in jet mills etc. – are also widely used at present for increasing the mobility of polymer chains. The most effective method of acting upon solids is processing in high-pressure apparatus such as Bridgeman anvils: the substance to be treated is submitted to plastic deformation with degrees
of deformation up to $10^3 - 10^4$ times under the action of a pressure of up to 1 GPa. As was shown previously, many polymers become almost completely amorphous in these conditions (Ref. 8). Moreover, the amorphous phase of polymers undergoes considerable rearrangement, i.e. ordering of the polymer chains takes place, with formation of a mesomorphic structure. In cases when the process of conversion to the amorphous state is incomplete, considerable impairment of structure is observed in the crystalline phase, with formation of a large number of defects. These changes in the structure of polymers are accompanied by a sharp increase in mobility already starts to appear at temperatures 100-120°C below the glass transition temperature, whereas for polypropylene it was established that, owing to the high degree of imperfection of the polymer crystal, the mobility of the polymer chains in the crystalline phase approaches the mobility of the chains in the amorphous phase (Refs. 9-13).

The creation of ultrafine pores in the polymer matrix increases the structural stability of a composite of polymer + active addition (lithium salt) because of intensive interphase interaction, which will prevent “bleeding” of the latter out of the polymer matrix. The highest mobility of the charge carriers is observed at the phase boundaries, therefore the motion of the charge carriers will increase in intensity as the phase boundary becomes more developed.

Accordingly, it was of interest to investigate the properties of SPE obtained as a result of intensive mechanical action – plastic deformation of a polymer/ lithium salt mixture under high pressure.

EXPERIMENTAL

The polymers used in this work were polysulphone, polyphenylene oxide, polycarbonate, polyethylene and cellulose. A mixture of polymer and lithium perchlorate was processed in equipment of the Bridgeman anvil type under a pressure of 1 GPa at room temperature; anvils of VK6 hard alloy were used, with diameter of the working surfaces 20 mm; the angle of rotation of the anvils was 300°. As a result, polymer disks 100 µm thick were obtained. Then they were ground to powder with particle size of 20-30 µm, from which plates were compacted with dimensions of 2.0 by 2.0 cm and thickness of 30-50 µm. Next they were held in a drying cabinet for 12 hours at 100°C. The electrical conductivity of the polymer electrolytes was investigated using a type R-5021 a.c. bridge. The cell was made of polypropylene, and the electrodes were of platinum. The thickness of the polymer electrolyte was varied from 50 to 100.0 µm. The cell is connected to the bridge with screened leads. A series of measurements was taken for each sample: from 3 to 5 tests each time, then the mean value was calculated.

The discharge and polariation characteristics of lithium electrodes in the Li-PE-Li system were investigated in a three-electrode cell made of polypropylene. One of the lithium electrodes was placed at the bottom of the cell, the polymer electrolyte was above this, and a second Li electrode was placed on top. The working surface of the electrodes was 4 cm². A spring ensured that the electrodes made contact uniformly with the polymer electrolyte. An Li/Li⁺ electrode was used as the reference electrode. The electrochemical characteristics of the lithium electrodes were investigated with the well-known three-electrode circuit using a PI-50-1 potentiostat and a PR-8 programmer in galvanostatic mode. The potential of the electrodes was measured using a V-7-40 volt meter.

RESULTS

Table 1 shows the results of measurements of the conductivity of SPEs based on various polymers. It can be seen that all the composites are characterised by high conductivity properties, which greatly exceed (by 2-3 orders of magnitude) the best foreign products of this kind, and are on a par with liquid electrolytes. Among the materials presented in Table 1, the composite with polysulphone as the polymer constituent stands out, therefore only this SPE was investigated further.

<table>
<thead>
<tr>
<th>Table 1. Conductivity of solid-polymer electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designation</td>
</tr>
<tr>
<td>Polyphenylene oxide + 15% LiClO₄</td>
</tr>
<tr>
<td>Polysulphidesulphone + 20% LiClO₄</td>
</tr>
<tr>
<td>Polystyrene + 20% LiClO₄</td>
</tr>
<tr>
<td>Cellulose + 20% LiClO₄</td>
</tr>
<tr>
<td>Polycarbonate + 20% LiClO₄</td>
</tr>
</tbody>
</table>

The studies showed that the electrical conductivity of the SPE depends on the concentration of lithium perchlorate in the polymer. It was found that the electrical conductivity of the SPE passes through an extremum as the concentration of lithium salt is increased. The maximum electrical conductivity is achieved at a salt concentration of 1.1-1.2 mol/l. Further increase in its concentration leads to impairment of electrical conductivity. The SPEs investigated are characterised by uniformity of properties: conductivity is independent of layer thickness.

The studies revealed that the losses at the polymer electrolyte/lithium interface are 30-60 mV and gradually decrease during charging and discharging, which can be explained by “running-in” of the component parts of the
Li-SPE system as they adapt to one another. As shown in Figure 1, the magnitude of the contact losses increases with increase in viscosity of the polymer.

Micrographs of the surface of the lithium foil were obtained before and after cycling. Examination of these showed that it had not been changed significantly.

Two variants of batteries with an anode of metallic lithium are currently being used:

• with a liquid electrolyte, modified with a special additive to prevent dendrite formation (Ref. 15);
• with a solid-polymer electrolyte.

A modified liquid electrolyte is being employed successfully at the Energiya company in batteries in which lithium-vanadium bronze is used as the active substance of the cathode. Comparative tests were conducted in the present work with a cathode based on lithium-manganese dioxide spinel. As shown in Figure 2, initially a battery with a liquid electrolyte, with which the separator was impregnated, has some advantage with respect to voltage, which may be connected with smaller contact losses at the electrode-electrolyte boundary. However, starting from just the 5th cycle of charging and discharging, the battery with the solid-polymer electrolyte has higher voltage throughout discharging. This result is due to two effects. On the one hand the SPE “adapts” to the electrodes, and the ohmic losses at the phase boundary decrease. On the other hand, as can be seen in Figure 3, this is associated with impairment of the anode polarisation characteristic in the battery with a modified liquid electrolyte. This can be explained by the fact that, by the 5th cycle, a particular kind of film forms on the surface of the lithium. This film has a certain ohmic resistance, which is maintained during subsequent charging and discharging. It is the presence of this film that ensures stable discharge of a battery of this type, as it prevents the formation of dendrites on the surface of the lithium anode. Thus, the gain in voltage of the battery with a polymer electrolyte is connected with lower anode polarisation.

Figure 1. Voltage losses at the Li-SPE phase boundary as a function of polymer viscosity. 1 – $\eta = 0.32 \text{ dl/g}$; 2 – $\eta = 0.50 \text{ dl/g}$; 3 – $\eta = 0.44 \text{ dl/g}$

Figure 2. Discharge characteristic of batteries with polymer and liquid electrolytes. Discharge current density: 0.5 mA/cm$^2$. Series 4 – 1st cycle with liquid electrolyte (LE), Series 3 – 1st cycle with PE, Series 2 – 30th cycle with PE, Series 1 – 30th cycle with LE.

Figure 3. Discharge characteristics of anodes of batteries with polymer and liquid electrolytes. Discharge current density: 0.5 mA/cm$^2$. Series 1 – LE – 5th cycle, Series 2 – PE, Series 3 – LE – 1st cycle.

Figure 4 shows the charging-discharging characteristics of the battery at different current densities. They show that the battery has high energy parameters in the range $i = 0.25-1.5$ mA/cm$^2$.

Prototypes of the battery were tested over 250 cycles at charge-discharge current density of 0.5 mA/cm$^2$ in the voltage range 2.5-4.0 V. Cycling efficiency was 95-98%. The results of the experimental studies showed that the decrease in energy characteristics of the battery is connected with cathode losses.

An experimental batch of batteries of standard type CR2325 was manufactured, and these are undergoing tests at the experimental station of the Energiya company. Several variants of the batteries were used:

• with a liquid electrolyte,
• with a solid-polymer electrolyte.
The batteries were discharged to a constant resistance of 1.8 Ω. The charging current is 1.4 mA. The results of tests on batteries from an assembled batch are shown in Table 2.

Comparing the results, it can be seen that, as with the prototype battery, the advantages of SPEs are apparent from the 5th to the 7th charge-discharge cycle.

CONCLUSIONS

An SPE based on polysulphone has been developed, and is superior to existing similar products with respect to electrical conductivity. It is very stable, is inert with respect to the electrodes and ensures reversibility of the charging-discharging process of a metallic lithium anode. An experimental batch of batteries of the standard type CR2325 was produced with a solid-polymer electrolyte, and tests showed they have advantages over batteries with a modified liquid electrolyte.

This work was undertaken within the framework of the scientific-technical project “University research in priority areas of science and technology” of the Ministry of Defence of the Russian Federation (Project code: 205.03.01.002).

REFERENCES

2. F.M. Gray: Polymer electrolytes. USA, 1993, 244 pp.
15. Organic electrolyte EPIEL-5P. TU 3252.005.39825716-96.

<table>
<thead>
<tr>
<th>No.</th>
<th>Liquid electrolyte</th>
<th>Solid-polymer electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, h charge</td>
<td>T, h disch.</td>
</tr>
<tr>
<td>1</td>
<td>26.0</td>
<td>4.23</td>
</tr>
<tr>
<td>3</td>
<td>26.0</td>
<td>4.21</td>
</tr>
<tr>
<td>5</td>
<td>26.0</td>
<td>4.25</td>
</tr>
<tr>
<td>7</td>
<td>26.0</td>
<td>4.36</td>
</tr>
<tr>
<td>15</td>
<td>25.8</td>
<td>4.34</td>
</tr>
<tr>
<td>27</td>
<td>25.9</td>
<td>4.32</td>
</tr>
<tr>
<td>53</td>
<td>26.1</td>
<td>4.3</td>
</tr>
<tr>
<td>250</td>
<td>26.0</td>
<td>4.44</td>
</tr>
</tbody>
</table>

Figure 4. Charge-discharge characteristics of batteries at different current densities. Series 1 – i = 0.25 mA/cm², Series 2 – i = 0.50 mA/cm², Series 3 – i = 0.75 mA/cm², Series 4 – i = 1.5 mA/cm².