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Microporous polymer films as separators for lithium-ion batteries

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New microporous polyethylene, polypropylene and polyvinylidene fluoride films have been elaborated as separators for lithium-ion batteries. The samples were obtained by a technique based on polymer melt extrusion. Investigation of the batteries in the mode of charge-discharge cycles was carried out. It is shown that these porous materials match or exceed performance characteristics of commercial separators "Celgard 2400". It was found out that the usage of polyethylene separators allows preventing emergency situations which may be induced by an uncontrollable temperature increase during the battery operation.

Keywords: polyethylene, polypropylene, polyvinylidene-fluoride, separator, lithium-ion battery.

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Lithium-ion batteries find a wide application in portable and self-contained electric devices due to their small sizes, low self-discharge and absence of the „memory effect". In the battery operation, the key role is played by a separator that divides the space between the cathode and anode and allows the passage of electrolyte. The main requirements for the separators [1,2] are inertness to other battery materials and through permeability enabling the ion transport. In the case of lithium-ion batteries, there is an additional requirement: the separator should prevent the growth of lithium dendrites during the battery charging. The advantages of polymer films used as separators are their high chemical resistance to aggressive media including electrolytes, good mechanical properties (breaking strength and elasticity), and small thickness ($15-30\,\mu$m).

An alternative to conventional film separators are polymer-fiber nonwovens. As compared with the film separators, they possess a higher specific bulk electric capacity and lower electric resistance [3,4]. However, they have a disadvantage, namely, low resistance to growth of lithium dendrites. In addition, nonwoven separators are as are rule inferior to the film separators in mechanical strength because of low density. In addition, the procedure of their fabrication is based on using organic solvents, which needs overcoming environmental issues associated with their regeneration and disposal. The prospects of film separators is associated with the possibility of using them in high-power batteries, since the oriented structure of such materials implies the film shrinkage under heating, which is followed by closing of pores and thus prevents overheating and spontaneous combustion.

In this work, the polymer-film separators were obtained using the technique based on polymer melt extrusion [5,6]. The manufacturing process is environmentally safe because it does not involve toxic substances and solvents. The electrolyte passage through the obtained samples is ensured by the existence of through flow channels in their porous structure. The technique is highly technological and cost-effective because of using standard plastic-processing equipment in producing the porous film. Actuality of the work is associated with the need to develop Russian technologies for producing materials necessary for wide-application devices for the purpose of substituting with them previously used imported analogues.

The goal of this work was to study and analyze the functioning of separators prepared of polyethylene (PE), polypropylene (PP) and polyvinylidene fluoride (PVDF) in lithium-ion batteries in comparison with polypropylene separators „Celgard 2400".

The porous films were produced from grades of polyethylene HDPE-276 (Stavrolen, Russia), polypropylene PPG-1035 (Stavrolen, Russia), and polyvinylidene-fluoride Kynar-720 (Atofina Chemicals, USA).

The film melting point was determined by differential scanning calorimetry (DSC 204 F1 Calorimeter, Netzsch). The sample thickness was measured with digital micrometer (Vogel 0-50x0.001). Overall porosity of the separators was calculated by the ratio between densities of the porous and dense films determined gravimetrically. The permittivity was determined via the ethanol flow rate through the porous film. The size and number of through flow pores was estimated by filtration porosimetry via the pressure dependence of the non-wetting liquid (ethanol:water mixture, 30:70) flow rate through the separator. Mechanical characteristics (strength) were measured at tensile-testing machine 2166 P-5 (Tochpribor, Russia) at uniaxial sample extension.

The obtained separators possess high overall porosity and are permeable to liquids and gases (see the Table). The films porous structure consists of both the pores closed in the film bulk and through flow pores. The separators permeability to electrolyte, which controls the battery internal resistance (and, hence, its efficiency), depends on the size

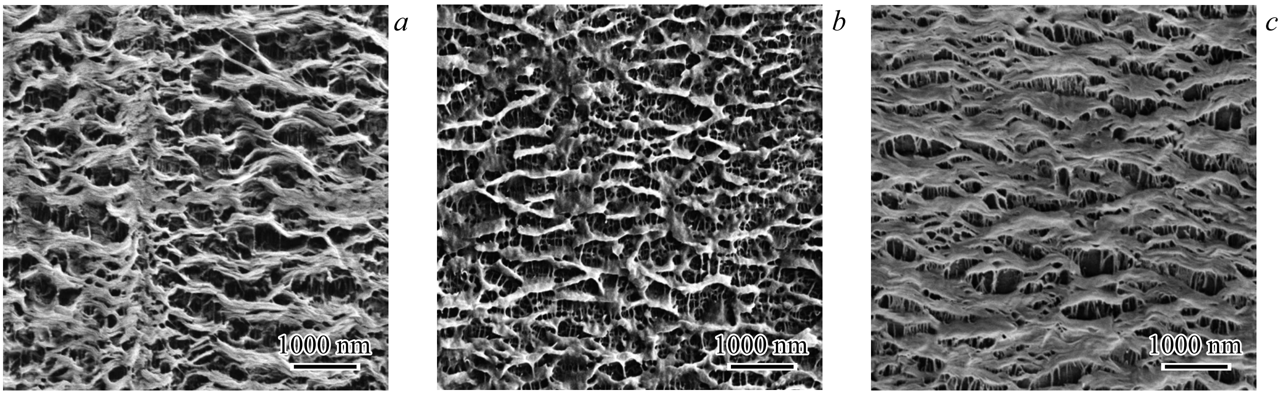

Figure 1. Electron-microscopy images of the surface of porous films prepared of PE (*a*), PP (*b*) and PVDF (*c*).

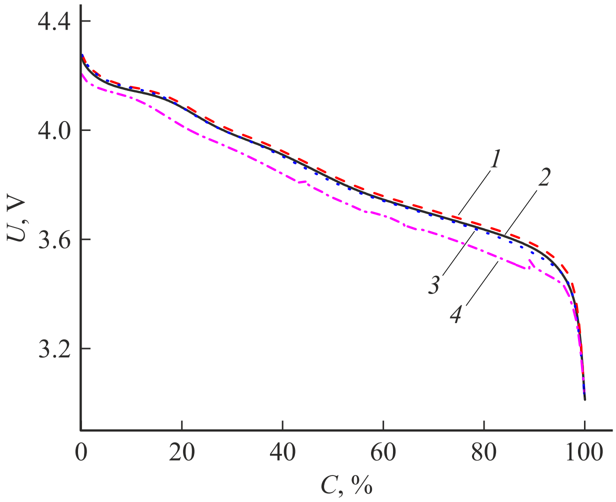

Figure 2. Discharge curves for batteries with separator „Celgard 2400" (*1*) and porous films prepared of PE (*2*), PP (*3*) and PVDF (*4*).

and number of through flow channels interconnecting the film surfaces. Mean sizes of through flow pores in the obtained materials are 180, 140 and 30 nm for the PE, PP and PVDF films, respectively. Since the PE film structure is characterized by the largest pores, their permeability is the highest. As the Table shows, permeability of the given PE and PP films to liquid is much higher than that of commercial analogue „Celgard 2400".

The through flow channels get formed due to interconnecting of closed pores, and, as a result, they have a tortuous shape due to which the lithium dendrite growth is inhibited. The mechanism for the through flow channels appearance [5,6] initiates the formation of a film surface relief (Fig. 1) manifesting the character of the internal porous structure.

To validate the possibility of using the proposed porous films as separators for lithium-ion batteries, they were placed in disk-shaped CR2032 prototype. As the cathode material, mixed oxide NCM811 was used, while the anode was made of metallic lithium. As the electrolyte, the 1M solution of $LiPF_6$ in a mixture of alkyl carbonates was used.

The disk prototypes were subjected to ten charge-discharge cycles in the ten-hour mode in the voltage range of 3.0 to 4.3 V. Fig. 2 presents voltage U of disk prototypes with different separators versus reduced capacity C for the second cycle. No degradation of the characteristics was observed during the ten cycles. The obtained data show that the PE and PP separators, as well as separators „Celgard 2400" exhibit identical performance with respect to discharge (Fig. 2). Reduction in the average discharge voltage for the batteries with PVDF separators may be explained by that its resistance in electrolyte is higher than those of the PE and PP separators; this is in a good accordance with the data on permeability presented in the Table.

Thus, being used as separators, all the considered porous films provide ion conductivity in batteries. Therewith, the PE and PP films ensure the battery performance comparable with that of foreign analogues and can successfully substitute them.

It is known that the commonly applied method for preventing thermal „acceleration" (uncontrollable overheating) of lithium-ion batteries is the use of PE separators able for „comelting" (closing through flow pores for electrolyte passage) at temperatures above 100°C [1,7]. To simulate emergency operation in the case of overheating, the disk prototype with the PE separator was forcedly heated during discharge. As Fig. 3 shows, a sharp decrease in voltage is observed at the temperatures of about 130°C, which is due to blocking the ion conductivity. In the case of the battery self-heating due to passing of electric current (for instance, short-circuit current), „comelting" of the PE separator results in opening the electric circuit and thus in preventing the emergency situation (combustion).

Thus, performance characteristics of the microporous films obtained in this study match foreign analogues and may be used as separators in producing lithium-ion batteries so as to ensure their operational efficiency and safety. Development of techniques for this production will contribute

Characteristics of porous polymer separators

Characteristic	PE	PP	PVDF	„Celgard 2400“
Melting point, °C	132 ± 1	172 ± 1	168 ± 1	165
Thickness, μm	16 ± 2	33 ± 2	20 ± 2	25
Overall porosity, %	39 ± 3	38 ± 3	28 ± 2	41
Permeability to liquids, l/(m^2 · h · atm)	120 ± 20	60 ± 10	0.7 ± 0.1	8.7
Breaking strength, MPa	110 ± 10	130 ± 10	140 ± 20	142

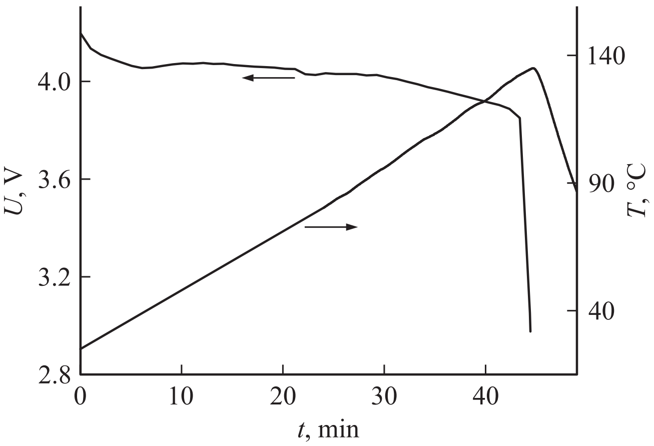

Figure 3. Time dependence of voltage of the disk prototype with the PE porous film as a separator during the external heating.

to solving the problem of substituting imported components with domestic materials.

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Conflict of interests

The authors declare that they have no conflict of interests.

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