

Article

Long-Term Cycling Behavior of Electrospun Separators for Lithium-Ion Batteries: A Comparison with Conventional Separators

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Abstract: This paper considered the electrochemical behavior of new electrospun separators for lithium-ion batteries on the basis of nano- and microfibers of polyvinylidene fluoride (PVDF) and its polymer composition, with polytetrafluoroethylene (PTFE) having advanced electroconductive properties over conventionally used separators based on polypropylene (PP) and glass-fibers (GF). Such advancement is associated with the low density of electrospun material leading to lower mechanical strengths. However, its use in the electrochemical systems with middle-voltage anode materials where dendrite growth is excluded is very prospective. The performance at the operation of the separators were investigated in the three-electrode-containing laboratory half-cells having $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the electrode under investigation. Galvanostatic charge and discharge tests of cells were conducted under variation of the experimental conditions: the current varied in the range 0.1 C–1 C, and 1C cycling was conducted over 100 cycles. The working electrode and separator characteristics at cycling were monitored by the electrochemical impedance spectroscopy (EIS) method. The gradual decrease of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ transport characteristics at cycling was noticed for all the types of separators. However, the least degradation rate was associated with the PVDF and the PTFE-based separator. This fact is explained by the better conductivity of an electrospun separator compared to others, with therefore a better current distribution on the electrode surface and a lower concentration perturbation in the electrode.

Keywords: lithium-ion battery (LIB); separator; electrospun materials; polyvinylidene fluoride (PVDF); polypropylene (PP); glass-fibers (GF); polytetrafluoroethylene (PTFE); lithium titanate; galvanostatic charge and discharge; C-Rate; diffusion coefficient of lithium ions (D); electrochemical characteristics

1. Introduction

Lithium-ion batteries are widely used to power portable electronic devices, aerospace systems and more recently, electric vehicles and stationary energy storage systems, due to their high specific energy and power, their significant working resource and wide range of operating conditions. The main components of a lithium-ion battery are the active materials of electrodes, electrolyte and the separator. The function of the separator in the lithium-ion battery is very important: it prevents the direct electronic contact of the electrodes, ensuring the exchange of lithium ions between them. Significant efforts have been applied to improve separators: the goals are to reduce the thickness of the separator, to increase the wettability of the electrolyte solutions, to increase the mechanical strength and to provide a programmable behavior of the separator in the emergency operation of the battery, for example, blocking ion exchange at rapid heating. One of the significant characteristics of lithium-ion batteries is their ability for long-term cycling whilst maintaining a stable capacity and a shape of charge–discharge

curves at various currents. The separator can play a noticeable role in this ability. The improved cycling behavior of a LiMn_2O_4 -electrode [1] in a half-cell with a metal Li counter electrode and a 1M LiPF_6 electrolyte in a mixture of organic solvents was demonstrated in which a separation material, based on electrospun polyvinylidene fluoride (PVDF)-hexafluoropropylene (HFP) and its modifications with silicon (IV) oxide, was used as a separator in comparison with a polypropylene-based separator. The authors [2] presented a comparison of the electrochemical behavior of LiFePO_4 electrode in a half-cell with a metallic Li-electrode, where a polysulfone-amide/polyacrylonitril/polysulfone-amide multilayer material was used as a separator, which was of minimal resistance and demonstrated an improved performance during long-term cycling compared to a commercial PP separator. In other works, electroformed PVDF-based separation materials with ceramic nanoparticles based on SiO_2 [3] and Al_2O_3 [4] were obtained. Thus, the cycled capacity of the LiMn_2O_4 electrode after 100 cycles in a half cell with a metallic Li electrode and an experimental separator according to [4] turned out to be 10% higher than under the same conditions with a commercial polypropylene (PP) separator. According to the data of [5,6], separator materials having high porosity values obtained by the electrospinning method markedly improved the electrochemical behavior of the studied electrodes. All the listed examples of separators relate to the capillary electrospinning method. In our previously published work [7], it was shown that the capillary-less electrospinning method allowed to obtain a separator based on the PVDF | polytetrafluoroethylene (PTFE) polymer composition having a high porosity of 71.4% and an electrolyte wettability of 800% using 0.67 M LiClO_4 electrolyte in a mixture of propylene carbonate (PC) and dimethoxyethane (DME). This made it possible to obtain improved characteristics of the specific charge–discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode in a cell with a metallic Li electrode at various currents from 0.1 C to 25 C compared to the similar cell where commercial PP-based separator was used.

Along with polymer separators, glass-fiber (GF) separators are also used in lithium-ion batteries. They are characterized by a high thermal stability, strength and chemical inertness, which determines their high working life in the battery [8]. One of the disadvantages of such separators is the rather large pore size of more than 1 μm , which practically excludes protection against a short circuit due to the formation of dendritic lithium. Another disadvantage is the relatively large thickness of the material, which consequently increases the resistance to the transfer of lithium ions between the electrodes. The authors [9] reported obtaining a glass fiber separator having fairly good physical characteristics: thermal stability at 150 $^\circ\text{C}$, a relatively small thickness of about 45 μm and an electrolyte wettability of 200%–300%. As a result, the specific discharge capacity of the LiFePO_4 electrode in a half cell with a metallic Li electrode and the mentioned separator after the 100th cycle is 10% higher than the value obtained in a similar cell with a commercial Celgard2400 separator.

To summarize what has been said here, the main problems in lithium storage systems that the separator is designed to solve what follows. First of all, this is a possible growth of dendrites on the anode—needle-shaped lithium crystals, which can form at potentials close to the potential of a lithium metal electrode. Dendrites, as they grow, are able to puncture the separator and short-circuit the electrodes. Separator developers are trying to create a separator structure that can prevent dendrites from germinating. For this purpose, the separator must have a dense finely porous structure. However, such a structure creates significant resistance to electric current. On some anodes, the formation of dendrites is fundamentally impossible, for example, on $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In the absence of this problem, the structure of the separator can be optimized in order to increase the conductive properties. This especially concerns electrochemical systems in which power is a priority. These systems also include the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. The fibrous electrospun structure of the separator on the basis of polymeric PVDF|PTFE composition is best suited to the characteristics of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode.

This paper presented the results of a comparative study of the electrochemical properties of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode in a half-cell with a metallic Li-electrode, an 0.67 M LiClO_4 electrolyte in the mixed solvent composed of PC and DME (7:3), as well as one of the separators: an electrospun separator based on the polymeric PVDF|PTFE composition described in [7], commercial PP material and GF

material. A difference in the change in the electrochemical properties during long-term cycling of the cell depending on the used separation material is shown. Among the analyzed electrochemical characteristics of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode were the following: cycled capacity, average working voltage, and also parameters found as a result of an analysis of the electrochemical impedance spectra, including the diffusion coefficient D of lithium ions in the electrode material.

2. Materials and Methods

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ active electrode material was synthesized by solid state reaction with preliminary mechanochemical activation pretreatment. The initial chemical precursors were as follows: titanium (IV) oxide TiO_2 of crystalline modification rutile (purity qualification «pure», producer «Lenreaktiv», Russia), carbonate of lithium Li_2CO_3 (purity qualification «pure», producer «Neva-Reaktiv», Russia), used for the synthesis of the lithium titanate electrode material ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) in a stoichiometric ratio.

The reaction blend was mechanically activated in the AGO-2 planetary ball mill (Novits, Russia). Steel drums filled with 6 mm steel balls were used. Acetone was used as a dispersion medium. The mixture of reagents was treated during 20 min at a spin rate of 560 rpm.

The annealing of the ground reactant blend was conducted in a tube furnace under the argon atmosphere at the rate temperature increasing of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. After turning off the heating the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ product was cooled together with the furnace. Our approach to the producing of lithium pentatitanate was based on our earlier work [10]. The use of an inert atmosphere during heat treatment to obtain $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was an excessive measure, since this material was stable both in an inert or reducing atmosphere and in an oxidizing one. In the vast majority of works, it was the oxidizing (air) atmosphere that was used in the synthesis of this material, since such conditions were easier to create. However, there are examples of obtaining this material in an inert atmosphere [11], when a carbon additive was introduced into the reaction mixture for synthesis, which subsequently increased the electronic conductivity of the electrode material. In our case, an inert atmosphere was preferable for the operation of the annealing furnace in order to exclude the possible ingress of unwanted impurities into the annealing zone. At the same time, this did not affect the composition and the characteristics of the resulting material.

The separator based on the nanofibers mix of PVDF|PTFE was produced using a capillary-less electrospinning process fed by the polymeric solution with the application of the NS LAB-200 equipment (producer «Elmarco», Czech Republic). The PVDF and PVDF|PTFE copolymers were dissolved in the solvent mix of dimethylformamide (DMF) and butylacetate (BA) in a proportion of 1:1 by weight at constant mixing during 2 h to obtain polymeric solutions of the concentrations of >8 wt.%. The polymeric solution was immersed in an electrospinning bath. The electrospinning process was conducted in accordance with the following optimal conditions: the collecting electrode consisted of one string, the supplying electrode consisted of four strings, the inter-electrodes distance approached 170 mm and the electrode spin rate was 16 rpm. Paper was used as a substrate to obtain a defective-less structure of the separator. The operation voltage was 70 kV, current was 0.02–0.03 mA, the humidity and the temperature during the process conducted in the NS LAB-200 were $14\% \pm 2\%$ and $25\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$, respectively. The thicknesses of the separators were measured using the thickness gauge Absolute Digimatic ID-S 543-790 (producer «Mitutoyo Corp.», Japan). The fiber thicknesses of the separators were measured by scanning electron microscopy (SEM) using a MIRA LMU microscope (producer «Tescan», Czech Republic).

The electrolyte uptake (EU) of the separator was measured by soaking the PVDF|PTFE, PP and glass fiber membranes in 0.67 M LiClO_4 electrolyte in the mixture of PC:DME = 7:3 (by vol.), which was calculated in accordance with Equation (1):

$$EU(\%) = \frac{w_1 - w_0}{w_0} \times 100, \quad (1)$$

where w_0 and w_1 designate the separator weight preceding and following the soaking in the electrolyte for 1 h, respectively.

The working electrode was prepared by mixing 80 w% active material $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 10 w% acetylene black conductive additive and 10 w% PVdF polymer binder. The electrolyte composition was a 0.67 M LiClO_4 solution in PC: DME (7:3, vol.). The electrode slurry was cast on the Al-foil with a coating density of $5 \text{ mg}\cdot\text{cm}^{-2}$ by «Dr. Blade» technique. The electrochemical tests were performed in pouch cells containing the electrode under testing, the lithium counter electrode and the lithium reference electrode. An Elins/P-45X potentiostat/galvanostat with FRA module (Elins, Russian Federation) and an Autolab/PGSTAT302N modular high-current potentiostat/galvanostat (ECO CHEMIE, Netherlands) with a FRA frequency response analyzer were used for the electrochemical impedance spectroscopy (EIS) measurements. The measurements were carried out in the frequency range 1 mHz–100 kHz and the electrode response was measured in two limiting states—completely lithiated and delithiated at different stages of cycling in the galvanostatic charge–discharge mode, similar to what was done in our earlier work [7]. Neware/BTS10V10mA (Neware Technology Limited, China) and Booster/UZR 0.03–10 (Booster, Russian Federation) charge–discharge modules were utilized for the galvanostatic charge–discharge tests. C-rate tests of the cells with different samples of the separator were performed by galvanostatic charge and discharge in a series of subsequently applied normalized currents of 0.1C, 0.2C, 0.5C, 1C. The current value C was taken based on the theoretical capacity of the material $175 \text{ mAh}\cdot\text{g}^{-1}$. The electrode potentials hereafter were given versus a Li reference electrode in the same solution. All the electrochemical measurements were carried out at under 25 °C.

3. Results

3.1. Structural Characterization of the Electrospun PVDF|PTFE, Conventional PP-Based and Glass Fiber Separators

Some structural features of the electrospun PVDF|PTFE and the conventional PP-based separators were thoroughly considered in our previous work [7]. Figure 1 demonstrates a comparison of the SEM images of typical samples of the electrospun (a), conventional PP-based (b) and glass fiber (c) separators. The glass fiber-based separator that we studied had a rather large thickness of 112 μm and a surface density of 35–40 $\text{g}\cdot\text{m}^{-2}$ and at the same time, a low strength in comparison with the separators based on PVDF|PTFE and PP. The average glass fiber diameter was significantly superior to that of the electrospun PVDF|PTFE material: 1.07 μm versus 0.200 μm . The porosity value for the glass fiber material was 81%, and the LiClO_4 electrolyte wettability value was at the level of 818%. For comparison, the separators based on PP and PVDF|PTFE had the following physical characteristics, respectively: porosity 39% and 71.4%, thickness 20 μm and 50 μm , wettability with LiClO_4 electrolyte of 445% and 800% [7].

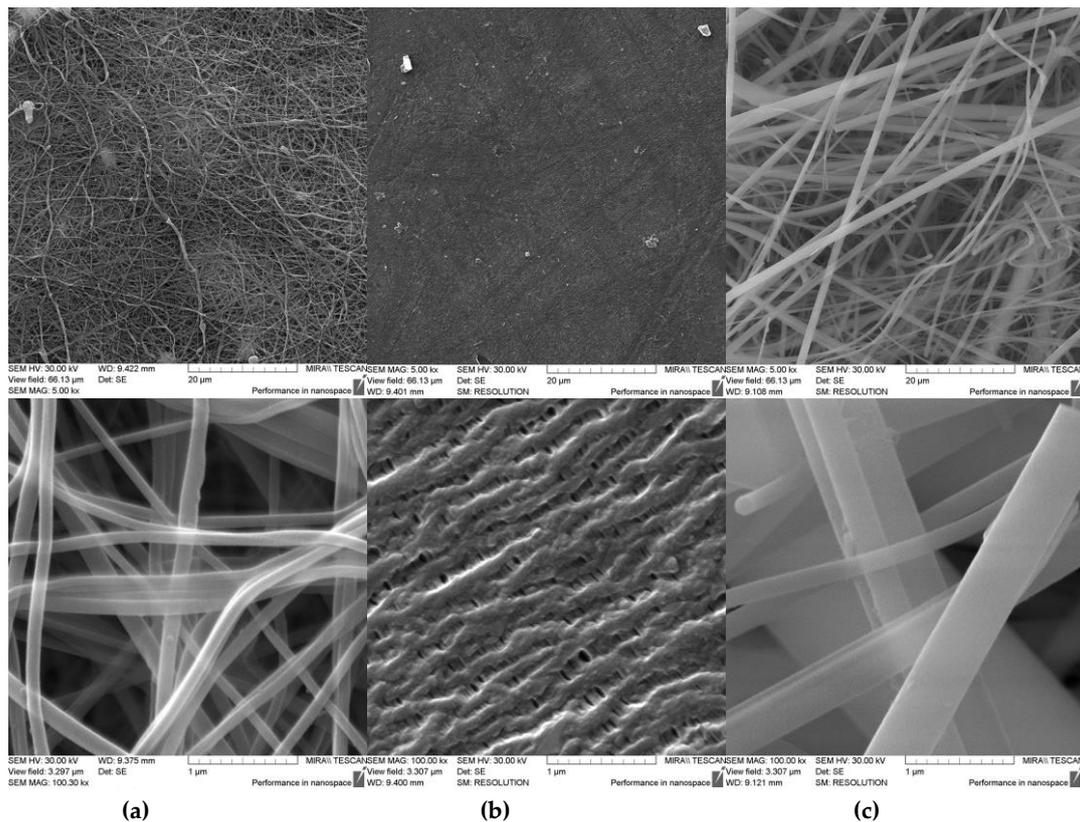


Figure 1. SEM micrographs of the: (a) polymer electrospun separator based on the polyvinylidene fluoride (PVDF)|polytetrafluoroethylene (PTFE) mix fibers, (b) the polypropylene (PP)-based separator; (c) the glass fiber-based separator.

3.2. Comparison of Cycling Performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Electrode in Half Cells with Electrospun PVDF|PTFE, Conventional PP-Based and Glass Fiber Separators

Figure 2 demonstrates the cathodic and anodic chronopotentiograms measured in the constant current mode when the value of the current consequently increases in the first four cycles from 0.1 C to 1 C and then resides at 1 C level up to 100 cycles for the cells containing three types of separators. Cells with an electrospun PVDF|PTFE separator demonstrated higher C-rates with respect to the cells with conventional separators on the basis of PP and glass fibers: at equal currents, bigger capacities during the long-term cycling of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode were observed.

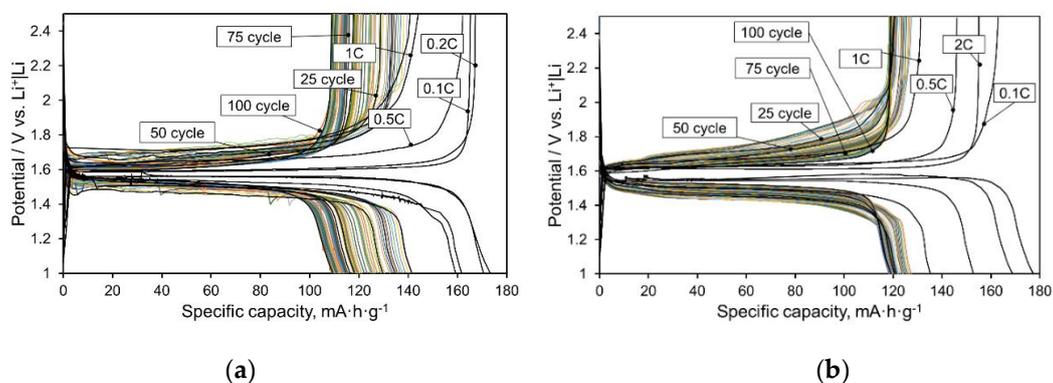


Figure 2. Cont.

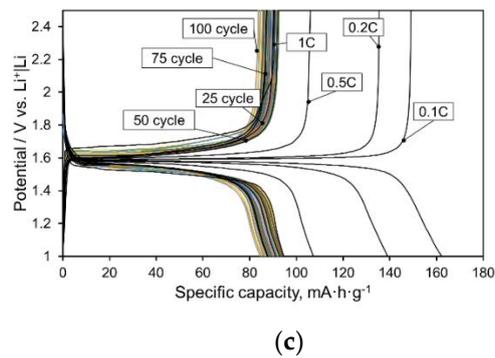


Figure 2. Constant current cathodic and anodic chronopotentiograms of the electrode on the basis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ when the value of the current consequently increases in the first four cycles from 0.1 C to 1 C and then resides at 1 C level up to 100 cycles for the cells containing three types of separators: (a) the electrospun PVDF|PTFE mix fiber-based separator; (b) the separator on the basis of PP; (c) the glass fiber separator.

Table 1 demonstrates the cathodic and anodic capacities and the mean electrode potentials in each mode, corresponding to the polarization of the electrode: an increase in the mean potential of the cathodic curve or a decrease in the mean potential of the anodic curve lead to higher electrode polarization, corresponding to the worsening of the C-rate capability. Considering these results, we can confirm that the electrospun separator on the basis of PVDF|PTFE fibers leads to a higher electrode C-rate capability than the glass fiber separator and the conventional separator on the basis of PP.

Table 1. Specific capacity, C , and the mean working electrode potential, E_{av} , the values for the constant current cathodic and anodic chronopotentiograms of the lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode when the value of the current consequently increases in the first four cycles from 0.1 C to 1 C and then resides at 1 C level up to 100 cycles for the cells containing three types of separators: (a) the electrospun PVDF|PTFE mix fiber-based separator; (b) the separator on the basis of PP; (c) the glass fiber separator.

(a) PVDF PTFE Mix of Fibers Separator						
No cycle	Current, C	Lithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V	Current, C	Delithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V
1	0.1	173.32	1.509	0.1	165.22	1.601
2	0.2	170.57	1.533	0.2	167.22	1.614
3	0.5	161.67	1.474	0.5	162.13	1.686
4	1	159.24	1.500	1	144.03	1.804
25	1	129.67	1.441	1	128.83	1.727
50	1	118.12	1.489	1	117.78	1.671
75	1	116.41	1.491	1	116.06	1.662
100	1	109.30	1.498	1	109.12	1.640
(b) PP-Based Separator						
No cycle	Current, C	Lithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V	Current, C	Delithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V
1	0.1	177.31	1.500	0.1	163.01	1.653
2	0.2	168.87	1.529	0.2	155.14	1.622
3	0.5	152.84	1.472	0.5	146.05	1.641
4	1	135.28	1.474	1	131.29	1.701
25	1	121.30	1.435	1	120.84	1.757
50	1	120.63	1.450	1	120.50	1.720
75	1	119.09	1.478	1	119.03	1.667
100	1	119.07	1.499	1	118.98	1.645
(c) Glass Fiber-Based Separator						
No cycle	Current, C	Lithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V	Current, C	Delithiation $C, \text{mA}\cdot\text{h}\cdot\text{g}^{-1}$	E_{av}, V
1	0.1	162.26	1.536	0.1	149.00	1.601
2	0.2	139.20	1.530	0.2	135.47	1.608
3	0.5	107.24	1.524	0.5	105.98	1.636
4	1	94.67	1.482	1	90.67	1.733
25	1	91.13	1.506	1	90.24	1.665
50	1	92.77	1.505	1	92.20	1.653
75	1	87.53	1.500	1	87.08	1.665
100	1	87.82	1.503	1	87.37	1.656

A more detailed assessment of the electrochemical behavior during the long-term cycling of the cells with tested samples of separators can be carried out using the dependences of the cycled capacity on the cycle number (Figure 3). The electrospun PVDF|PTFE mix fiber-based separator exhibited a higher level of capacity and higher cycling rate characteristics in the initial cycles compared to the PP-based separator material, and especially compared to the glass fiber separator material. However, the capacitance degradation rate of the electrospun PVDF|PTFE mix fiber-based separator was higher than that of the PP-based separator and the glass fiber separator. Since the composition of the active electrode material, the auxiliary components of the electrode mass, electrolyte and counter electrode was the same in all the cases, only the current and polarization distribution in the cell could influence the electrochemical characteristics. Since the resistance of the electrolyte in the pores of the separator was lower, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode in the cell with the PVDF|PTFE separator operated in a more intense mode and more fully realized its characteristics than in cells with the PP-based separator and the glass fiber separator. The degradation processes were also more intense, which is quite natural.

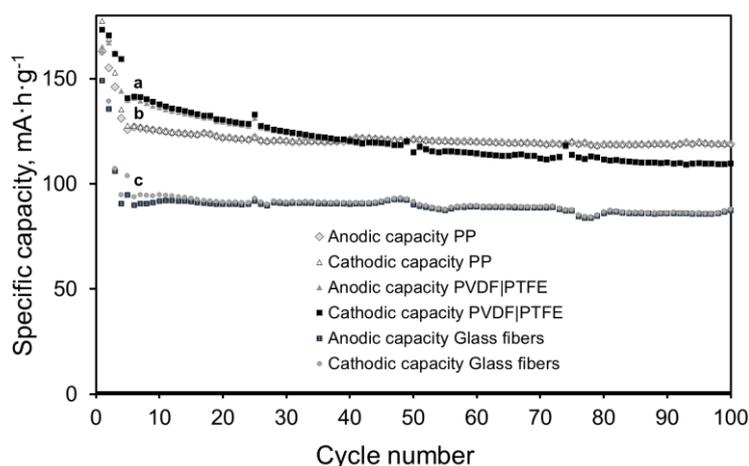


Figure 3. Dependence-specific capacity from the number cycle of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode when the current varies in the interval from 0.1 C to 1 C for the cells with three types of separators: (a) the electrospun PVDF|PTFE mix fiber-based separator (b) the PP-based separator; (c) the glass fibers separator.

3.3. EIS Measurements of Half Cells Containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Working Electrode, Metallic Li Counter and Reference Electrodes with the Separators on the Basis of Electrospun PVDF|PTFE Fibers, Glass Fibers and Conventional Separator on the Basis of PP

Figure 4a–g demonstrates the dependences of the parameters of the electrical equivalent circuit elements of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode on the different cycling current values from 0.1C to 1C and on the cycle number at the current of 1C. The electrochemical impedance spectra were measured at different stages (cycle number) of the long-term galvanostatic cycling of the cells with three types of separators: PVDF|PTFE, PP and glass fiber, in two stages: lithiated and delithiated. The electrical equivalent circuit (Figure 4h) for the spectra analysis was taken from our previous work [7].

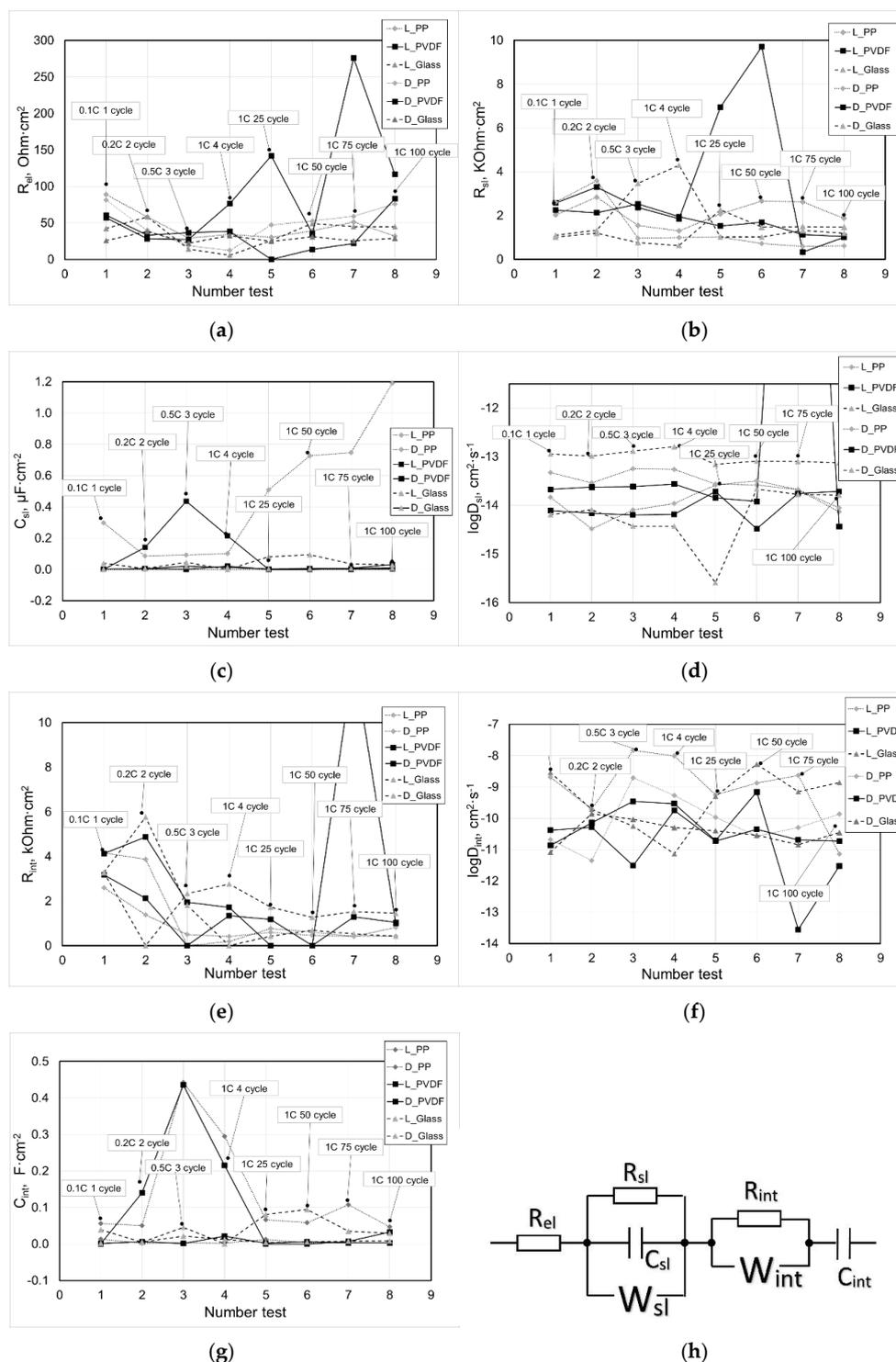


Figure 4. The dependences on the cycle number and the cycling current of the electrical equivalent circuit parameters found at the modelling of the electrochemical impedance spectroscopy (EIS) spectra of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode in the lithiated (L) and the delithiated (D) states, measured in the three-electrode pouch cells containing three types of separators: the electrospun PVDF|PTFE mix fiber-based separator (PVDF), the PP-based separator (PP) and the glass fiber separator (Glass): (a) the electrolyte + separator resistance, R_{el} ; (b) the surface layer resistance, R_{sl} ; (c) the surface layer geometry capacitance, C_{sl} ; (d) the surface layer lithium diffusion coefficient, D_{sl} ; (e) the intercalation layer (bulk) resistance, R_{int} ; (f) the intercalation layer (bulk) lithium diffusion coefficient, D_{int} ; and (g) the intercalation layer (bulk) intercalation capacity, C_{int} ; (h) the electrical equivalent circuit, used for the impedance spectra analysis.

4. Discussion

Nowadays, polymer separators with a non-fibrous structure, the basis of which, as a rule, is polypropylene, are widely distributed and characterized by their low porosity and wettability by electrolyte [12]. The dense structure of such separators reduces the likelihood of the formation of dendrites from lithium metal, however, this factor reduces the electrochemical characteristics of the electrodes. Fibrous separators create a much lower resistance to ion flow due to their higher porosity and wettability with electrolyte, however, their strength is much lower and therefore they are not suitable for use with electrode materials on which lithium dendrites can grow. For materials on which dendritic formation is impossible, like $\text{Li}_4\text{Ti}_5\text{O}_{12}$, they are quite suitable. In addition to polymeric fiber separators like the electrospun PVDF|PTFE mix fiber-based separator, there are also inorganic materials such as the glass fiber separator discussed in this article. Their structures have common features (Figure 1): the fibers are much thicker and less frequently located, but the space between the fibers is smaller, which explains the close values of porosity. The rheological properties of the fibers are also different: the glass fibers are more fragile, therefore to give the material strength it is necessary to increase its thickness, which we observed in the case of the glass fiber separator. Obviously, the structure of the separator will also affect the electrochemical characteristics of the electrodes. Earlier in [7], we compared the electrochemical characteristics of the electrodes in combination with the separators on the basis of the electrospun PVDF|PTFE fibers and on the basis of PP in terms of their ability to maintain high charge–discharge rates of electrodes. However, the effect of the separator type on the characteristics of the electrodes during the long-term cycling remained unexamined, which was the subject of this work.

Figures 2 and 3, as well as Table 1, show the data of galvanostatic cycling of half cells with all the tested samples of separators. The test mode consisted of two stages: 1) cycling at the current varying in the range 0.1 C–1 C; 2) long-term cycling at the current 1 C. The electrospun PVDF|PTFE mix fiber-based separator demonstrated superior capacity in the first stage of cycling during current increase. The capacity of the PP-based separator and the glass fiber separator significantly dropped when the current increased. This indicates a significantly lower ion flow resistance, which creates a PVDF|PTFE separator in comparison with the PP and especially with the GF separators. The observed sharp decrease in the capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode with an increasing current in the series 0.1C–1C in cells with the above two types of separator indicates a high ionic resistance of the electrolyte in the pores of the separator. This was due to several factors, including a small pore size and consequently, a relatively small effective cross-section of the electrolyte layer between the electrodes; as well as the poor wettability by electrolyte in the case of the PP separator, and therefore a small amount of retained electrolyte in the pores and possibly part of the broken conduction channels that were not completely filled with electrolyte; and finally, a greater thickness in the case of a GF separator, which increased the length of the conduction channels. At the same time, the higher stability of capacity was during the long-term cycling, the lower was this capacity. This phenomenon is associated with the different redistribution of polarization in the cell: in the series of PVDF|PTFE → PP → GF separators, the fraction of polarization per the electrolyte in the separator increased and the fraction per electrode decreased. Because of this, the concentration gradient decreased over the depth of the particles of the electrode material and the capacity extracted from the electrode was smaller. However, the smaller the fraction of the extracted lithium capacity, the softer the mode of operation of the electrode material was and the less degradation effects occurred.

To diagnose the state of the electrode material, the EIS method was used. The approach that was previously developed by us [7,13,14] was applied to the analysis of the impedance spectra (Figure 4). For the different initial values of the resistance of the electrolyte and the separator R_{el} for most of the samples of the separators, the tendency for its change during cycling was similar: at the first stage (current change 0.1 C–1 C), the values decreased, after which over 100 cycles the values returned to the previous level. Only the cell with the PVDF|PTFE sample measured after lithiation showed periodic sharp resistance jumps. Perhaps this was due to the strong nonequilibrium conditions at the interface of

the electrode, electrolyte and separator, since the main fraction of the polarization fell on the electrode. The resistance of the surface layer of the electrode R_{s1} monotonically decreased throughout the cycling. This was probably due to the development of ion conduction paths in the surface layer during cycling. The geometric capacitance of the surface layer of the electrode C_{s1} for most samples varied slightly, except in cases in which nonequilibrium conditions arose at the interface of the electrode, electrolyte and the separator, which apparently affected the dielectric constant of the surface layer. The diffusion coefficient of lithium ions in the surface layer D_{s1} also practically did not undergo changes during cycling, with the exception of sharp jumps in nonequilibrium conditions. The resistance of the bulk of the intercalation material R_{int} related to electron transfer tended to decrease during cycling, probably due to an increase in the defectiveness of the structure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compound. The diffusion coefficient of the lithium ions in the intercalation material D_{int} and intercalation capacity C_{int} , as the most sensitive parameters to the state of the electrode material, showed a noticeable scatter of values due to the nonequilibrium conditions. However, the general trend of their change was practically not observed.

Thus, long-term cycling at a moderate current (1 C) does not significantly affect the transport properties of an $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, in comparison with the effect of cycling in extreme current modes [7]. A possible reason for the dependence of the degradation rate of the electrode capacity on the type of separator material used is a different degree of nonequilibrium of cycling conditions due to the redistribution of polarization in the cell between the electrode and electrolyte in the pores of the separator.

5. Conclusions

A comparative study of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode electrochemical behavior in half cells with the electrospun PVDF|PTFE mix fiber-based, the PP-based and the glass fiber separators for lithium-ion batteries was considered. The behavior of cells during cycling at an increasing current from 0.1 C to 1 C and further long-term cycling by a constant current of 1 C was studied. The increase in the initial cell capacity in the series PVDF|PTFE \rightarrow PP \rightarrow GF separators and the decrease in the rate of capacity degradation in the same series were explained by the fact that the fraction of polarization per the electrolyte in the separator increased and the fraction per electrode decreased. That is why the concentration gradient decreased over the depth of the particles of the electrode material and the capacity extracted from the electrode was smaller. However, the smaller the fraction of extracted lithium capacity, the softer the mode of operation of the electrode material, and the less degradation effects occur. The conductive properties of the electrolyte in the pores of the separator and the nature of the polarization distribution in the cell are interpreted from the point of view of the structural characteristics of the separators. Using the EIS method, the electrode was diagnosed at various stages of cycling tests. It was found that long-term cycling at a moderate current (1 C) does not significantly affect the transport properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, in comparison with the effect of cycling in extreme current modes. The difference in the rate of the degradation of the capacitance during the prolonged cycling may be due to a different redistribution of polarization in the cell.

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