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Chemistry

DEVELOPMENT OF MEMBRANES BASED ON POLYVINYLIDENE FLUORIDE FOR LITHIUM BATTERIES

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Abstract. Two methods for producing lithium-conductive polymer films based on polyvinylidene fluoride (PVDF) were studied: saturating a dielectric PVDF film with a lithium-conductive solution and incorporating a lithium-conductive solution into a PVDF solution, followed by the fabrication of a lithium-conductive film. A comprehensive set of electrophysical studies on the properties of the proposed gel-polymer electrolyte across a wide temperature range (20–70 °C) and frequency range (0.1 Hz – 32 MHz) was conducted. Li-ion battery prototypes constructed using the engineered membrane exhibit improved performance and enhanced stability during charge / discharge cycling compared to cells with a commercial Celgard 2400 separator.

Keywords: polymer membrane, polyvinylidene fluoride, lithium-ion batteries.

1. Introduction

In the past decade, lithium-ion batteries (LIBs) have become an integral part of everyday life for humanity. They power mobile devices, electric vehicles, and store energy from solar panels and wind turbines[1]. The growing demand for more efficient, safe, and durable batteries is driving research efforts to explore new and improve existing components of LIBs. One area receiving intensified attention from scientists and engineers is solid, polymer, and gel electrolytes[2, 3]. These materials have found application not only in solid-state lithium or lithium-ion batteries but also in other electrochemical devices such as supercapacitors and electrochemical sensors. Research on polymer electrolytes was first initiated by Fenton *et al.* in 1973, and was later continued by the team led by Armand *et al.*, several years later[4]. These authors suggested that crystalline complexes formed from alkali metal salts and polyethylene oxide (PEO) could exhibit acceptable ionic conductivity, emphasizing their potential application as electrolytes in LIBs.

One method to enhance the ionic conductivity of electrolytes is through the use of gel, which combines the advantages of liquid and polymer electrolytes. Gel electrolytes are typically formed by retaining a certain amount of liquid electrolyte within a polymer framework. This framework acts as a medium to maintain the physical form of the electrolyte, while the percolated liquid medium facilitates the transport of lithium ions. The use of such a system eliminates the need for a conventional polymer separator, allowing all components of the LIB, both electrolyte and electrodes, to be laminated using existing coating technologies[5]. The main advantages of this class of electrolytes include:

1. Suppression of dendrite growth: The use of non-porous polymer membranes, which do not contain free pathways for electrolyte solution, is one successful approach to addressing lithium dendrite growth. This is significant because dendrite growth typically occurs in spaces where electrolytes can freely move[6].

2. Enhanced resistance to electrode volume changes during cycling: Polymer electrolytes, being more flexible than solid electrolytes made from inorganic glass or ceramics, can accommodate the volume change of electrodes during lithium-ion intercalation / deintercalation. This property is particularly beneficial in solid-state batteries using new anode materials based on tin and silicon, as it helps to oppose these volume changes.

3. Reduced Reactivity with Metallic Lithium: It is established that none of the solvents used in LIBs are thermodynamically stable with metallic lithium[7]. Gel electrolytes, with their lower solvent content, are expected to exhibit reduced reactivity compared to liquid electrolyte counterparts, mitigating risks associated with solvent-lithium reactions.

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4. Improved Safety: The solid-state battery structure, incorporating a gel-polymer electrolyte, offers increased resistance to impacts, vibrations, and mechanical deformations. Furthermore, gel electrolytes, due to the absence (or significantly reduced presence) of free solvent, exhibit higher thermal stability and are less prone to ignition. This significantly enhances the safety profile of batteries employing these electrolytes.

A large number of polymer electrolytes have been investigated, mostly based on PEO[8], polyacrylonitrile (PAN)[9], polymethyl methacrylate (PMMA)[10], polyvinyl chloride (PVC)[11], and polyvinylidene fluoride (PVDF)[12]. Among the advantages of PVDF are its high electrochemical stability, attributable to the strong electron-accepting functional group -C-F, and a high dielectric constant ($\varepsilon = 8.4$). This promotes the ionization of lithium salts, thus providing an acceptable concentration of charge carriers[13, 14]. These benefits, along with PVDF's ability to form homogeneous hybrid films with lithium salts in aprotic solvents, led to our choice of this polymer for membrane fabrication. However, the properties of the films, both mechanical and physicochemical, cited in the literature vary significantly depending on the grade of PVDF used, the solvents employed, film preparation conditions, their composition, *etc*.

To enhance the ionic conductivity of the electrolyte, a 1 M $LiClO_4$ solution in propylene carbonate (PC) was introduced into the PVDF membrane. Although lithium-ion batteries with various types of solvents, such as ethers, lactones, polymers, solid oxides, and ionic liquids, have been developed, commercial batteries mostly use organic carbonate solvents. For example, ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) are commonly used[15, 16]. These solvents have high dielectric properties (EC has a dielectric constant of 89.78, while PC has 64.92 at room temperature)[17], making them viable options for electrolytic applications as they contribute to a long service life for the battery[18]. The conductivity of these organic electrolytes is much lower than that of aqueous or protonic electrolytes, but their properties facilitate commercialization and stability with metallic lithium[19].

Lithium perchlorate ($LiClO_4$) is one of the most common lithium salts used in lithium-ion batteries[20, 21]. This salt is relatively stable to hydrolysis compared to $LiPF_6$ or $LiBF_4$, simplifying the battery manufacturing process. Moreover, unlike $LiPF_6$ or $LiBF_4$, the use of $LiClO_4$ does not result in the formation of HF, which leads to the degradation of electrode materials and electrode corrosion[22]. Marom *et al.* showed that $LiClO_4$ possesses many properties comparable to those of the significantly more expensive $LiPF_6$[23]. Furthermore, by using $LiClO_4$ instead of $LiPF_6$ or $LiBF_4$, the formation of toxic fluorine-containing compounds due to uncontrolled thermal reactions can be avoided[24].

The aim of this study was to develop a technology for obtaining lithium-conductive PVDF films, to study the electrophysical properties of the obtained films over a wide temperature range (20–70 °C) and frequency range (0.1 Hz – 32 MHz), to create a prototype LIB, and to investigate its charge/discharge characteristics.

2. Experimental

2.1. Materials

During the fabrication of lithium-conductive films, commercial PVDF grade KF 1100, with a molecular weight of 1100 from Kureha Corporation, was used, with N,N-dimethylacetamide serving as the solvent. The concentration of PVDF solution in N,N-dimethylacetamide was 10 wt. %. A 1M $LiClO_4$ solution in PC was employed as the lithium-conductive solution. A commercial sample of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC 622) manufactured by MTI Co was used as the cathode material.

2.2. Methods

The lithium-conductive PVDF film was obtained using two different methods:

The first method, as described[25], involves immersing a dry dielectric PVDF film in a lithium-conductive solution (1M $LiClO_4$ in PC). The dry dielectric PVDF film was prepared by dissolving PVDF granules in N,N-dimethylacetamide, followed by solvent evaporation at 85 °C for 24 hours in a drying oven (without vacuum). The resulting dry PVDF film was then placed in the 1M $LiClO_4$ solution in PC. The film's mass was periodically measured until it stabilized, indicating that saturation had been reached. Over five days at 20 °C, the PVDF film's weight increased by 0.007 g, corresponding to a 35.5 wt. % gain.

The second method for obtaining a lithium-conductive PVDF film, as outlined[26], involves simultaneously dissolving PVDF polymer in the solvent and adding the lithium-conductive component to the resultant solution. PVDF granules were dissolved in N,N-dimethylacetamide, to which a lithium-conductive solution (1M $LiClO_4$ in PC) was added. The resulting mixture was dried at 85 °C for 24 hours in a drying oven (without vacuum) to form the lithium-conductive film. The obtained films were used in the following measurements.

A composite solid electrolyte was prepared by incorporating $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) nanoparticles, with a NASICON structure synthesized *via* the sol-gel method, into a mixture of PVDF in N,N-dimethylacetamide and 1M $LiClO_4$ in PC. The mixture was then dried in a drying oven (without vacuum). The mass ratio of LATP nanoparticles to dry PVDF was 1:1.

The conductivity values of the film materials were determined from the results of complex impedance analysis. Impedance measurements were conducted using a Solartron SI 1260 impedance and amplitude-phase characteristics analyzer with a specialized attachment for studying film materials. IR spectra were obtained using a Shimadzu IRAffinity-1S IR-Fourier spectrometer (Japan).

Cells with lithium electrodes, specifically symmetric cells (Li / Li) and lithium batteries (NMC / Li), were assembled in a coin-type 2016 cell using the obtained membranes and a commercial separator, Celgard 2400. To assemble the cells, the separators were wetted with electrolytes: 1 M $LiClO_4$ in PC and a commercial electrolyte LP 71 (1 M $LiPF_6$ solution in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate with a mass ratio of 1:1:1). The volume of the electrolyte was 50 μL in symmetric cells (Li / Li) and 120 μL in lithium batteries (NMC / Li) to ensure complete wetting of the separator and cathode material. The performance of the laboratory-developed cells was compared with cells assembled using commercial materials, specifically the LP 71 electrolyte and Celgard 2400 separator, as these components are widely used in commercial batteries.

The fabricated composite solid electrolyte was investigated in laboratory LIB samples featuring two types of cathode materials: original NMC 622 and NMC 622 modified using the sol-gel method. The procedure for modifying the cathode material is detailed in reference[27]. Metallic lithium served as the anode.

Electrochemical studies were conducted using an automatic 32-channel ARBIN system, designed for investigating power sources (manufactured by Arbin Instruments Co., Texas, USA), at a current density of 0.15 mA/cm^2. The effective electrode area was 2 cm^2 (16 mm in diameter). For symmetric cells (Li / Li), the lithium deposition / stripping capacity was set at 1.5 mAh. The internal resistance of the symmetric cells (Li / Li) was measured using the current pulse method with an amplitude of 40 mA at a frequency of 1 kHz. Galvanostatic charge / discharge testing of the lithium batteries (NMC / Li) was performed at a cycling rate of 0.2 C within a voltage range of 2.5–4.25 V.

3. Results and Discussion

The results of the conductivity measurements for PVDF films are presented in Fig. 1. As shown in the Fig. 1, the PVDF lithium-conductive film produced by the first method exhibits low conductivity at 20 °C, measured at 10^{-6} S/cm. This film formation method has certain advantages, notably the absence of solvent during fabrication, which is known to negatively impact the electro-physical characteristics and discharge properties of prototypes. However, this method also presents several drawbacks, including the uncontrolled infiltration of the PVDF film by the lithium-conductive solution, low conductivity, and poor reproducibility. Currently, the effect of temperature on the degree of infiltration of the dry PVDF film by the lithium-conductive solution remains unclear. In contrast, the conductivity of the PVDF film obtained using the second method is significantly higher, on the order of 10^{-4} S/cm at 20 °C, surpassing that of the film produced by the first method. Consequently, we chose the lithium-conductive PVDF film developed by the second method to create LIB prototypes.

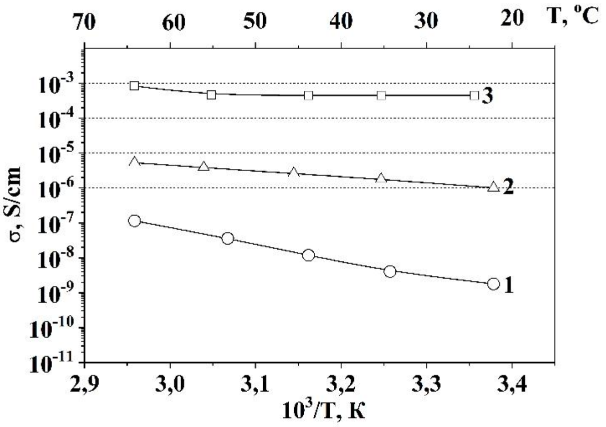

Fig. 1. Temperature dependence of conductivities: 1 – dry PVDF film; 2 – lithium-conductive PVDF film obtained by the first method; 3 – lithium-conductive PVDF film obtained by the second method

Figs. 2, *a* and *b* present the IR spectra of a dry PVDF dielectric film and a film wetted with a small amount of dimethylacetamide (5 μL), respectively. The spectrum of the dry film exclusively contains characteristic peaks of PVDF. The absorption peak observed at 1403 cm^{-1} is attributed to the vibrational modes of the CH_2 groups. The C–C stretching band of PVDF is detected[28] at 1185 cm^{-1}. Additionally, the peaks at 878 and 840 cm^{-1} are associated with the asymmetric stretching vibrations of the C–C–C backbone and the CF stretching vibrations within the PVDF matrix, respectively[29]. We also obtained the IR spectrum of the solvent-wetted film to verify the absence of solvent residues in the dry PVDF film. As observed in Fig. 2, *b*, after adding the solvent to the dry PVDF film, the characteristic peak of dimethylacetamide (approximately 1640 cm^{-1}) is evident in the IR spectrum. Analysis of the IR spectroscopy data presented in Figs. 2, *a* and *b* allows us to conclude that there is no residual solvent present in the dry PVDF film. Therefore, according to the results of IR spectroscopy, we claim that the proposed second method of fabrication successfully produces solvent-free membranes.

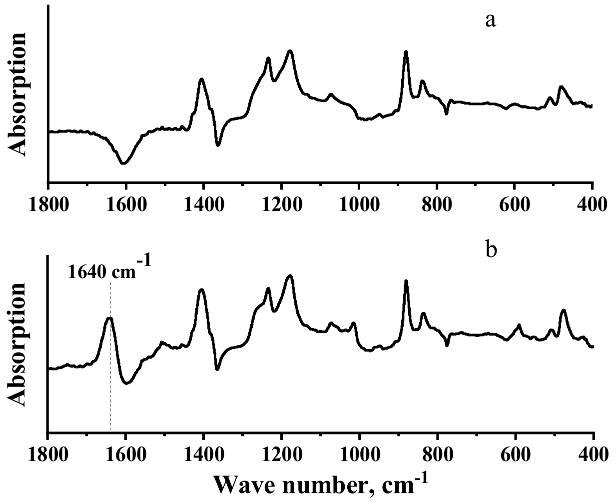

Fig. 2. IR spectrum of dry PVDF film (a) and PVDF film with added dimethylacetamide (b)

To investigate the stability of the obtained membrane during the lithium reverse deposition / dissolution, we assembled two types of symmetrical cells with lithium electrodes. One cell utilized a commercial separator, Celgard 2400, wetted with a commercial electrolyte, LP 71, while the other employed a PVDF membrane soaked in $LiClO_4$ dissolved in PC. Fig. 3 presents the voltage profiles of these cells during cycling. Fig. 3, *a* illustrates the voltage change over a range from 0 to 1600 hours, while Figs. 3, *b* and *c* focus on the intervals of 100–200 and 1100–1200 hours, respectively. As observed in the figures, at the beginning of cycling, both cells show a tendency for voltage decrease. However, the cell with the PVDF membrane exhibits a smaller change in polarization during cycling compared to the cell assembled with commercial materials.

Fig. 4 illustrates the change in internal resistance of cells with lithium electrodes during cycling. Resistance measurements were conducted by analyzing current pulses at a frequency of 1000 Hz. According to the test results, cells with PVDF-based membranes exhibit a significantly slower increase in internal resistance during cycling compared to cells with the Celgard 2400 separator. The internal resistance of cells with PVDF membranes increased from 11 to 56 Ohms by the 225th cycle, whereas for cells with the commercial separator and electrolyte LP 71, the resistance reached 47 Ohms by the 100th cycle. Furthermore, a sharp increase in cell resistance is observed after 100 cycles, indicating the poor cyclability of lithium with the Celgard 2400 separator. The data presented in Fig. 4 suggest that PVDF-based membranes can significantly enhance the cyclability of the lithium electrode.

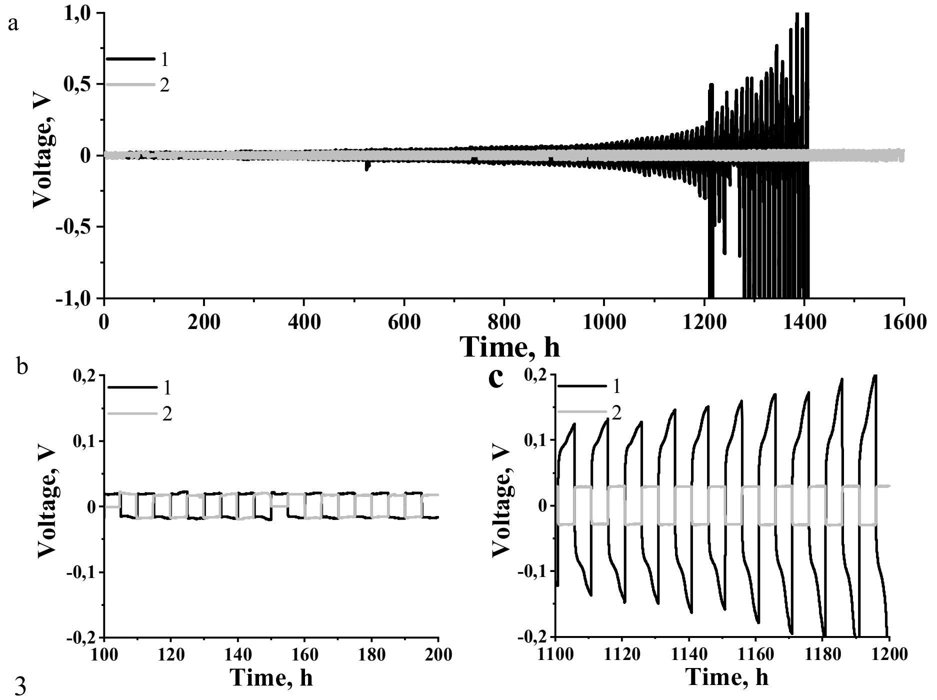

Fig. 3. Voltage profiles of cells with lithium electrodes during cycling in the intervals 0–1600 hours (a), 100–200 hours (b), and 1100–1200 hours (c): 1 – commercial separator Selgard 2400, 2 – PVDF membrane

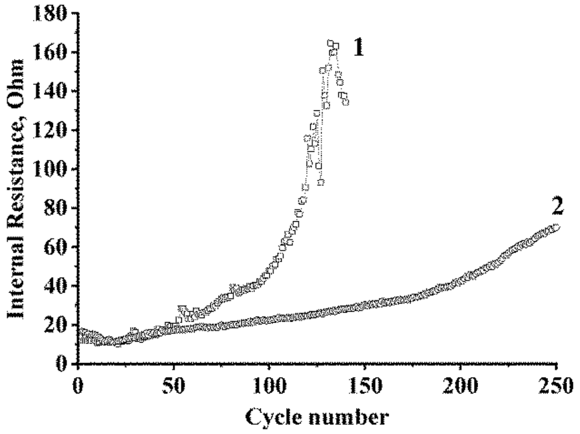

Fig. 4. Change in internal resistance of cells during cycling: 1 – with commercial separator Selgard 2400, 2 – with PVDF membrane

To evaluate the stability of charge / discharge characteristics of cells using different membranes, we performed cyclic tests of a lithium battery with NMC 622 cathodes. Fig. 5, *a* displays the galvanostatic charge-discharge curves for the first cycle. Although both types of cells demonstrate the same initial charge capacity (166 mAh/g), cells with a PVDF membrane exhibit a higher discharge capacity and, consequently, a higher Coulombic efficiency compared to those with a Celgard 2400 separator. Specifically, the discharge capacity for cells with the Celgard 2400 separator is 153.5 mAh/g, while for cells with a PVDF membrane, it is 159.15 mAh/g. The corresponding Coulombic efficiencies are 92.2 % and 95.8 %, respectively.

The change in internal resistance of lithium batteries with PVDF and Celgard 2400 membranes during cycling is presented in Fig. 5, *b*. We observed that lithium batteries with PVDF-based membranes soaked in a 1M $LiClO_4$ solution in PC exhibit a higher initial resistance compared to lithium batteries with a Celgard 2400 separator soaked in commercial LP 71 electrolyte. This difference is attributed to the lower electrical conductivity of the 1M $LiClO_4$ solution in PC compared to the commercial electrolyte LP 71 (24 *vs.* 13 mS/cm). The study primarily focused on comparing the changes in internal resistances of cells with different membranes throughout cycling.

As illustrated in Fig. 5, *b*, the internal resistance of cells with a PVDF membrane and Celgard 2400 separator monotonically increases during cycling. Notably, for the cell with the Celgard 2400 separator, a significant increase in resistance is observed after 150 cycles, indicating degradation in the lithium electrode's functionality for further charge / discharge cycles. These observations are consistent with the capacity *versus* cycle number relationship depicted in Fig. 5, *c*. Cells with different membranes show comparable initial charge/discharge characteristics, yet the half-cell with the PVDF membrane exhibits superior capacity retention throughout cycling. Specifically, as depicted in Fig. 5, *c*, the cell with the Celgard 2400 separator exhibits a rapid capacity decline after 175 cycles, whereas the cell with the PVDF membrane maintains performance beyond 200 cycles. Therefore, PVDF-based membranes offer several advantages over the commercial Celgard 2400 membranes and show promise for the development of lithium-ion batteries with high energy density.

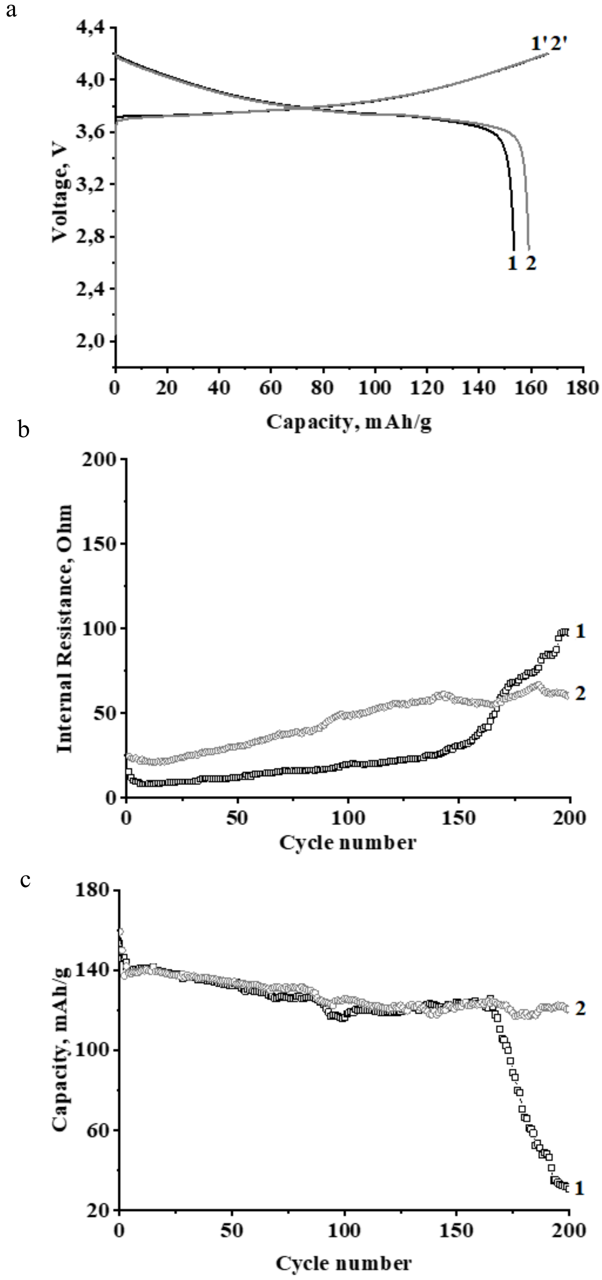

Fig. 5. Charge / discharge curves of the first cycles (a), change in internal resistance (b), and change in specific capacity (c) of lithium batteries: 1 – with commercial separator Selgard 2400, 2 – with PVDF membrane

Fig. 6, *a* presents the initial charge / discharge characteristics of laboratory cells featuring our fabricated composite solid electrolyte. According to the figure, both cells display similar initial charge capacities and discharge capacities, approximately 142 mAh/g. Meanwhile, as shown in Fig. 6, *b*, the cell with the modified cathode material demonstrates significantly lower internal resistance compared to the cell with the original cathode material. These findings lay the groundwork for further research aimed at optimizing the composition and manufacturing process of composite solid electrolytes based on PVDF and LATP, which will be explored in future studies.

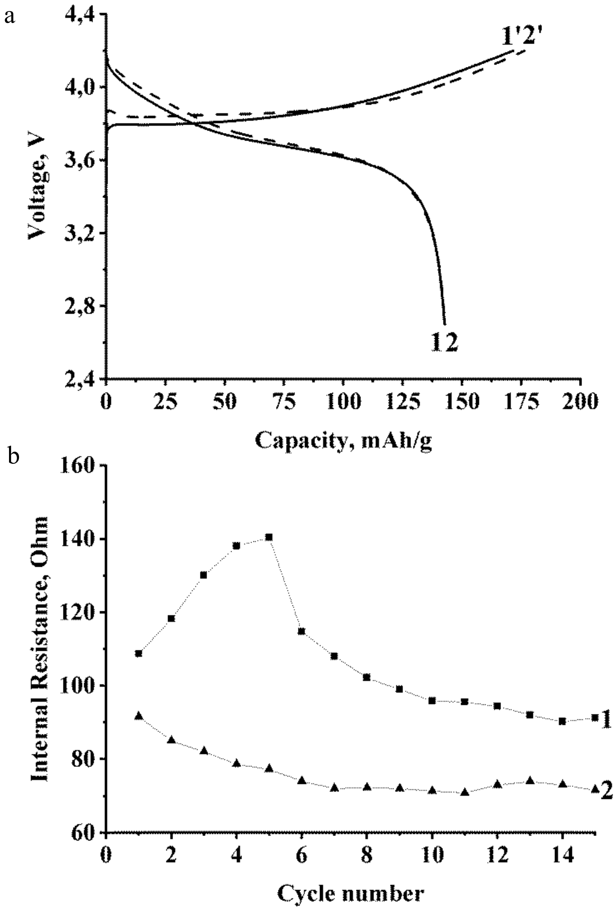

Fig. 6. Charge/discharge curves of the first cycles (a), and change in internal resistance (b) of LIBs prototypes: 1 – with initial cathode material, 2 – with modified cathode material

4. Conclusions

We have analyzed various methods of obtaining membranes based on PVDF. The results presented in this study demonstrate the potential of PVDF as a polymer matrix for separators in lithium-ion batteries. The PVDF membranes obtained can suppress the formation of lithium dendrites and improve the cycle life of lithium electrodes. Cells with PVDF membranes exhibit high stability in their characteristics during charge-discharge cycles. PVDF-based membranes possess the necessary qualities for the further development of a new generation of safe, solid-state batteries with high energy density.

The next stage of our research involves developing a fire-safe polymer electrolyte based on PVDF. This electrolyte will incorporate nanoparticles of a lithium-conductive oxide material $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ with a NASICON structure.

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РОЗРОБЛЕННЯ МЕМБРАН НА ОСНОВІ ПОЛІВІНІЛІДЕНФТОРИДУ ДЛЯ ЛІТІЄВИХ АКУМУЛЯТОРІВ

Анотація. *Досліджено два методи отримання літійпровідних полімерних плівок на основі полівініліденфториду (ПВДФ): насичення діелектричної плівки ПВДФ літійпровідним розчином і введення літійпровідного розчину в розчин ПВДФ із подальшим виготовленням літійпровідної плівки. Виконано комплекс електрофізичних досліджень властивостей запропонованого гель-полімерного електроліту в широкому температурному (20–70 °С) і частотному (0,1 Гц–32 МГц) діапазонах. Показано, що макети літій-іонних акумуляторів, побудовані із використанням розробленої мембрани, демонструють кращі характеристики та вищу стабільність упродовж заряд / розрядного циклування, ніж елементи з комерційним сепаратором Celgard 2400.*

Ключові слова: *полімерна мембрана, полівініліденфторид, літій-іонні акумулятори.*