

Polysulfone Copolymer as Polymer Electrolyte for Alkaline Fuel Cell and Li-Ion Battery Applications

¹S.E. Smirnov, ²N.A. Yashtulov, ¹I.A. Putsylov, ¹S.S. Smirnov, ²M.V. Lebedeva

¹“Moscow Power Engineering Institute”, National Research University, 111250 Moscow, Russia

²MIREA, Russian Technological University, 119571 Moscow, Russia

Abstract: Novel membranes and Solid Polymer Electrolytes (SPE) based on Polysulfone (PS) and Perfluorine diphenylolpropane (PFPP) copolymer were obtained and investigated as electrolytes for fuel cell and battery applications. Polymer materials were investigated by means of electron microscopy, EDSX and *in-situ* voltammetry methods. Alkaline membrane fuel cell with PS-PFPP/5% SiO₂ and PS-PFPP/5% CNT composite membranes were evaluated and showed promising performance. The obtained data shows that the PS-PFPP copolymer based SPEs for lithium-ion batteries have superior conductivity compared to the closest alternatives and which are stable during charge-discharge cycling.

Key words: Solid polymer electrolyte, alkaline membrane fuel cell, lithium, battery, hydrogen energy, electrochemical testing

INTRODUCTION

The modern energy including upcoming hydrogen energy requires the development of the new efficient on-site generation systems and energy storage systems. Electrochemical energy production is under serious consideration as an alternative energy/power source as long as this energy consumption is designed to be more sustainable and more environmentally friendly (Winter and Brodd, 2004).

Moreover, the use of electrochemical energy conversion devices or systems together with Renewable Energy Sources (RES) is relevant due to the variability of output power. The energy storage generated by small power plants for the subsequent smoothing of peak loads is very important task. In addition to small and large energy, there are significant demand for highly efficient power sources and batteries on transport, portable devices (cellphones, laptops, etc.), aviation, etc. (Nishizawa *et al.*, 2013; Wilberforce *et al.*, 2016; Pollet *et al.*, 2012).

Long-term energy storage in the form of hydrogen is especially, important for the power plants based on RES. The chemical energy stored in the form of gaseous hydrogen is environmentally safe and significantly surpass the capacity of traditional batteries despite the less performance of fuel cell/electrolyzer cycle (about 40 vs. 98% of Li-based batteries). It is important in case of permanent absence of energy from RES, for example, during the polar night and at no wind conditions.

To ensure the needs of distributed energy and portable applications in energy storage systems and power sources of different type and capacity hydrogen Proton Exchange Membrane (PEMFC) and Alkaline Membrane (AMFC) fuel cells with water electrolyzers and lithium-ion batteries are considered as the most suitable. These devices allow for direct and reverse conversion of electrical energy into chemical energy of hydrogen which can reduce not only daily but seasonal variations of RES energy output.

Solid polymer electrolyte is a crucial component of the both fuel cells and lithium-ion batteries (Winter and Brodd, 2004). Recent years have seen extensive research on the preparation and properties of anion exchange membranes including hydrocarbon alkaline membranes based on polysulfone (Merle *et al.*, 2011) which represent a cheaper alternative to the Nafion®-type commercial proton exchange membrane. There are many researches related to development of the hybrid polymer membranes with inorganic oxides and Carbon Nanotubes (CNT) as fillers for AMFC. For example, ZrO₂, TiO₂, SiO₂, Al₂O₃ are the well-known fillers for alkaline polymer hybrid membranes and the addition of hydrophilic nanosized powder fillers resulted in high ionic conductivity and wettability of alkaline hybrid polymer membranes (Vinodh *et al.*, 2011; Zhou *et al.*, 2009; Chen *et al.*, 2005; Devrim *et al.*, 2009).

Now a days batteries leading as an energy storage system in power plants based on RES and lithium-ion batteries successfully displacing lead-acid ones due to

their light weight, high energy and power density, longer lifespan (Diouf and Pode, 2015). Solid polymer electrolytes represent the ultimate in terms of desirable properties due to an all-solid-state battery construction, simplicity of manufacture, a higher energy density (Arico *et al.*, 2005). The solid polyelectrolytes consisting of polyester and lithium perchlorate are the most elaborated. However, these electrolytes have low conductivity ($10^{-5} \text{ S}\cdot\text{cm}^{-1}$) at room temperature and have found limited application. At present moment Polyethylene Oxide (PEO) is one of the most widely studied material for the Solid Polymer Electrolyte (SPE). It has many advantages such as low toxicity, high chemical and electrochemical stability, high local chain mobility, etc. PEO is well solvated polymer due to the high content of oxygen atoms which are the electron donor and have ability to ion-ion interaction (Arico *et al.*, 2005; Stephan and Nahm, 2006; Agrawal and Pandey, 2008; Smirnov *et al.*, 2001).

Both crystalline and amorphous phases were observed in PEO based SPEs. Usually the crystalline phase doesn't contain any salt and the amorphous one represents as a solution of salt in polymer and defines ionic conductivity providing the movement of ions and mobility of polymeric circuits. Therefore, the higher amorphous phase content leads to the increasing of SPE electrical conductivity. Whereas the amount of crystalline phase in SPE depends on numerous factors including the amount of salt impregnated into the polymer and its structure, i.e., cation size and charge (Stephan and Nahm, 2006). The crystalline phase content could be reduced by following methods: introduction of flexible blocks in polymer, introduction of elastomers in a matrix, PEO structuring, introduction of plasticizing agent, synthesis of new organometallic salts with low lattice energy and plasticizing properties (Arico *et al.*, 2005; Agrawal and Pandey, 2008; Smirnov *et al.*, 2001; Brissot *et al.*, 1998; Nishimoto *et al.*, 1998; Shukla and Thakur, 2011).

The introduction of flexible blocks is the least efficient method as the complex formation results in salts precipitation. The best results have been obtained by using polymer nanocomposites. SPE with the conductivity of about 10^{-4} - $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at room temperature were obtained using polypropylene oxide-polymethyl methacrylate (about 30%) composition. Injection of polyacrylonitrile-butadiene and polystyrene-butadiene in SPE copolymers alongside with electric conductivity increasing results in sharp worsening of film mechanical properties (Brissot *et al.*, 1998). Structuring of polymers SPE made from are more promising approach. Copolymers from polyethylene oxide triol and polyethylene oxide diisocyanate, from polypropylene oxide and phenyl isocyanate and from PEO radiationally-structured by

acrylate oligomer are the best examples of structuring polymers. However, electrical conductivity of this materials doesn't exceed $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ while it is quite difficult to obtain them (Nishimoto *et al.*, 1998). There are some papers in literature on a research of nanocomposite SPEs based on other polymers, for example such polymers as polymethyl methacrylate, polyethylene glycol-polyurethane-polyacrylonitrile or polietilenglikol-poliuretan-polymethyl methacrylate (Shukla and Thakur, 2011; Shah *et al.*, 2010; Chilaka and Ghosh, 2012). But electrical conductivity of such SPEs at room temperature even using introduction of nanoexcipients doesn't exceed $10^{-6} \text{ S}\cdot\text{cm}^{-1}$.

PS based SPE with a high electrical conductivity at room temperature ($10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and chemical stability was developed in National Research University "MPEI" early (Chebotarev *et al.*, 2004), so that, as a follow-up to the previous project presented work is devoted to SPE based Polysulfone-perfluorine diphenylolpropane (PS-PFPP) copolymer. Moreover, PS-PFPP was used as a functional matrix support for alkaline fuel cell membrane. According to some properties of this copolymer it may exceed the functional parameters of membranes based on other hydrocarbon polymers. The preparation and electrochemical testing of composite membranes using PS-PFPP as a matrix modified by CNT and SiO_2 as filler for AMFC was carried out.

MATERIALS AND METHODS

Synthesis of polymer materials: PS-PFPP copolymer was synthesized in Institute of Plastics named after G.S. Petrov, Russia (Kuleshov *et al.*, 2016). Hybrid alkaline copolymer PS-PFPP based membranes for AMFC testing were synthesized by PS-PFPP modification with SiO_2 , CNT. SiO_2 nanopowder ("Plazmoterm", 15-25 nm, Russia) and multiwalled carbon nanotubes with size of 10-15 nm ("Sigma Aldrich", USA) were used as fillers.

Membranes for AMFC were synthesized as follows. The PS-PFPP copolymer powder dissolved in Dimethylacetamide (DMAA). Suspensions of SiO_2 and CNT in DMAA were prepared separately. To obtain modified membranes SiO_2 (or CNT) suspension was added to the copolymer solution. Then hybrid membranes were immersed in deionized water at room temperature and dried at $60\pm 5^\circ\text{C}$. The solution with membranes were ultrasonicated for 3-7 min. Water diffused inside the membranes through the pores matrix structure. Finally, the hybrid membranes were dried at 60°C for 10 h and then at 40°C for 2 h in vacuum. The percentage of SiO_2 and CNT in the mixtures with PS-PFPP was varied from 2-10%. The membranes thickness was of $100\pm 10 \mu\text{m}$.

SPEs for lithium-ion batteries were prepared as follows: PS-PFPP polymer and LiClO_4 powders in calculated amounts were dissolved in DMAA, thoroughly mixed, poured into a mold coated with Teflon and placed in drying cabinet at a temperature of $60 \pm 5^\circ\text{C}$. Finally, SPEs with thickness of 10-20 μ and different LiClO_4 concentration were obtained.

Conductivity measurements: To investigate the AMFC membranes conductivity by electrochemical impedance spectroscopy a symmetrical cell with blocking electrodes made of stainless steel with active surface area of 2 cm^2 was used. The cell's impedance was measured at 20°C using Z-2000 (Electrochemical instruments-Elins, Russia) and frequency range of 10^{-1} - 10^5 Hz with a signal amplitude of 10 mV. To measure the conductivity, the PS-PFPP composite membranes with SiO_2 and CNT nanopowders were primarily placed in 1 M KOH solution for 10 h and then they were washed several times with deionized water. After the KOH removing, the membrane conductivity was measured. The conductivity of the PS-PFPP SPE for lithium-ion batteries was measured using the symmetric cell from polypropylene with the blocking lithium electrodes with surface area of 2 cm^2 .

AMFC preparation and testing: Gas diffusion layers were prepared as follows: 80 wt.% Vulcan XC-72 carbon black, 50 wt.% polytetrafluoroethylene (Sigma Aldrich, USA) solutions and double distilled water and isopropyl alcohol were mixed and ultrasonicated within 1 h. Then the obtained ink solution was coated onto the carbon cloth and dried in a vacuum oven at 80°C for 1 h and treated in furnace at 400°C for 4 h. Carbon black XC-72 supported Pt-Pd and Pt catalysts were prepared according to procedure discussed in Yashtulov *et al.* (2016a, b) with Pt/Pd molar ratio of 2:1 and metal loading of $0.3\text{ mg}\cdot\text{cm}^{-2}$ and $0.2\text{ mg}\cdot\text{cm}^{-2}$, respectively. PS-PFPP-based membranes prepared as described early were sandwiched between the prepared anode and cathode electrodes and hot pressed at 100°C and pressure of about 15 bars for 3 min.

The AMFC power density vs. current density curves and polarization ones were obtained using fuel cell test system 850°C ("Scribner Acc. Inc.", USA) station for small electrodes at different temperatures.

Lithium battery cell preparation and testing: For lithium cells the discharge and polarization curves were measured in Li-SPE-Li system in a three-electrode polypropylene cell. One of lithium electrodes was stacked on the cell bottom, the SPE was settled on it and the second electrode was placed on top. The active electrode surface area was of 1 cm^2 . The Li/Li^+ electrode was used as a

reference. The lithium electrodes energy parameters were investigated by means of three-electrode cell at 298 K using the Solartron SI 1287 electrochemical interface (Solartron Analytical, USA) with 1 M LiClO_4 concentration. Before and after battery cell cycling surface of lithium electrodes was investigated using JSM 5300 LV (JEOL, Japan) electronic microscope. Structure and morphology of SPEs were studied by X-Ray Energy Dispersive Spectroscopy (XEDS), Scanning Electron Microscopy (SEM) and Transition Electron Microscopy (TEM) methods using JSM-U3 scanning electron microscope (JEOL, Japan) equipped with a WinEDS attachment for X-ray microanalysis and EM-301 transmission electron microscope.

RESULTS AND DISCUSSION

AMFC testing: The power density vs. current density curves and polarization ones of AMFCs with PS-PFPP based membranes with different fillers are presented in Fig. 1 and 2. Fuel cell testing was carried out for H_2/O_2 fuel cells with PS-PFPP/5% SiO_2 , PS-PFPP/5% CNT composite membranes and pure PS-PFPP membrane at 25°C (Fig. 1) and 60°C (Fig. 2).

Table 1 presents the comparative performance data of the fuel cells with prepared membranes and well-known PS-based composite materials from literature (Vinodh *et al.*, 2011; Zhou *et al.*, 2009; Chen *et al.*, 2005; Devrim *et al.*, 2009). Table 1 analysis and electrochemical testing results show that copolymer PS-PFPP membrane modified by SiO_2 gives better performance than previously reported values for AMFC with PS-based composite membranes containing ZrO_2 , SiO_2 , CNT as fillers at 60°C (Vinodh *et al.*, 2011). PS-PFPP/5% SiO_2 membrane also show higher power density compared to the pure membrane and the membrane modified by CNT. PS-PFPP/5% SiO_2 membrane shows maximum conductivity of $1.92\cdot 10^{-2}\text{ S}\cdot\text{cm}^{-1}$. Such hybrid membrane nanocomposites have higher electrical conductivity in KOH solutions than PS-based materials with TiO_2 hydrophilic fillers (Yashtulov *et al.*, 2016a, b).

The analysis of the data presented on Fig. 1 and 2 and Table 1 allow to suggest that the PS-PFPP/5% SiO_2 composite membrane shows better performance compared to PS-PFPP/5% CNT one in terms of polarization curve and maximum power density at 25 and 60°C . The obtained results suggest the high degree performance of H_2/O_2 AMFC with PS-PFPP/5% SiO_2 polymer membranes. AMFC with PS-PFPP/5% SiO_2 composite membrane showed the maximum power density of $280\text{ mW}\cdot\text{cm}^{-2}$ at current density of $725\text{ mA}\cdot\text{cm}^{-2}$ at 60°C (Vinodh *et al.*, 2011). Therefore, SiO_2 is most promising hydrophilic filler compared CNT for PS-PFPP based composite membranes.

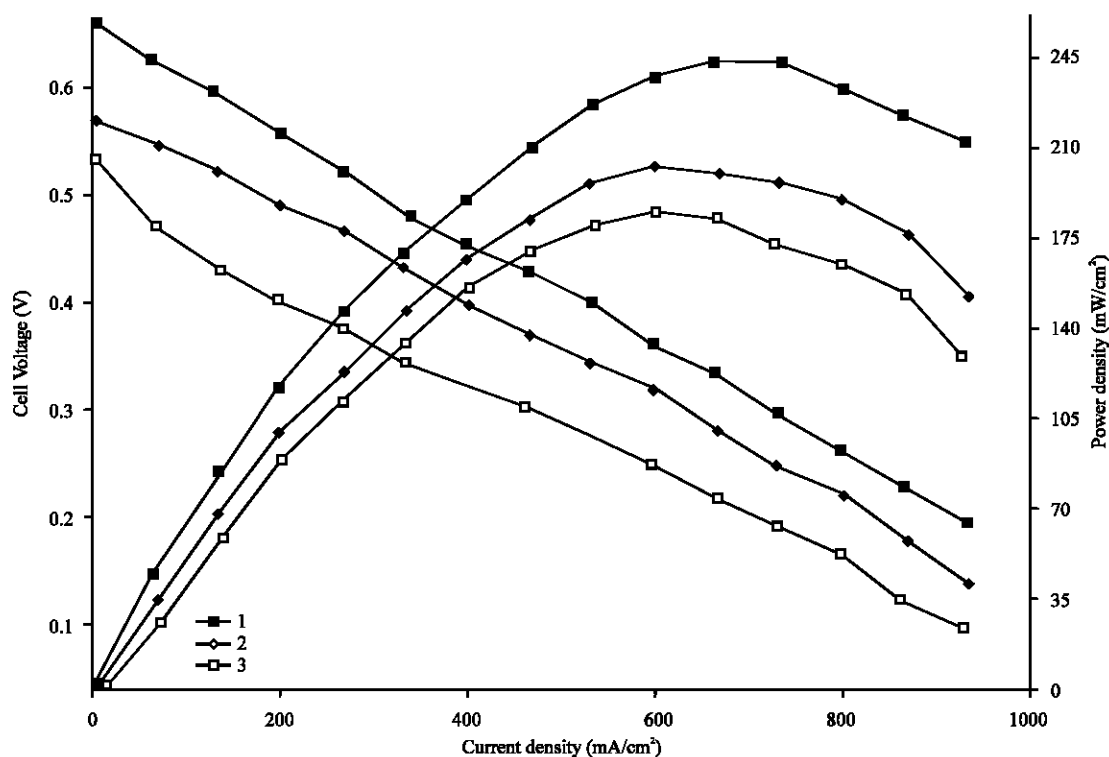


Fig. 1: Volt-and watt-ampere FC characteristics with PS-PFPP/SiO₂; 1) PS-PFPP/CNT; 2) Composite membranes and pure PS-PFPP and 3) Membrane at 25°C

Table 1: Electrochemical parameters of alkaline fuel cells based on PS (Vinodh *et al.*, 2011) and PS-PFPP based membranes modified with different fillers at 60°C

Membranes	Conductivity (S/cm)	Current density (mA/cm ²)	Power density (mW/cm ²)	Open circuit Voltage (V)
PS-PFPP/SiO ₂	1.92*10 ⁻²	725	280	0.86
PS-PFPP/	1.08*10 ⁻²	510	205	0.80
PS/SiO ₂	1.63*10 ⁻²	700	252	0.87
PS/ZrO ₂	1.51*10 ⁻²	500	175	0.7
PS/CNT	0.84*10 ⁻²	500	190	0.75

Lithium battery testing: The LiClO₄ concentration and polymer viscosity significantly influences the SPE electrical conductivity. The dependence of SPE electrical conductivity from LiClO₄ concentration in PS-PFPP and reduced viscosity are presented on Fig. 3. Figure 3 shows that the electrical conductivity is growing up with the rise of LiClO₄ concentration SPE and passes through maximum corresponding to 17% value of LiClO₄ concentration. The further increasing of lithium perchlorate concentration resulted in the SPE electrical conductivity decreasing. The polymer viscosity and molecular weight also essentially influence on electrical conductivity. The homogeneity of properties is inherent for investigated SPEs, so, the electrical conductivity doesn't depend on SPE thickness. The reversibility of the charge-discharge process in Li-SPE-Li system was investigated during 450 cycles. Discharge was carried out up to 100% of charge capacity

at current densities of 1.0-2.5 mA·cm⁻² and cycling depth of discharge up to 60 C·cm⁻². As shown in Fig. 4 the polarization sluggishly decreases from a cycle to a cycle, until a steady-state value will be reached: currently it has been occurred after 45-50 cycles (Fig. 4). The SPE electrical conductivity during the cycling process didn't change.

As the SPE represents by itself the salt solution in a copolymer matrix, it is necessary to expect that its greatest electrical conductivity should be reached at the highest homogeneity of system. According to the results of microscopic studies high homogeneity of SPE structure is reached at 17 wt.% LiClO₄ content and optimum synthesis conditions. XEDS and SEM analysis data are presented on Fig. 5. SPE samples contain estimated amount of LiClO₄ and are homogeneous and uniform at magnification up to ×3000. According to the TEM data (Fig. 6) the bulk of

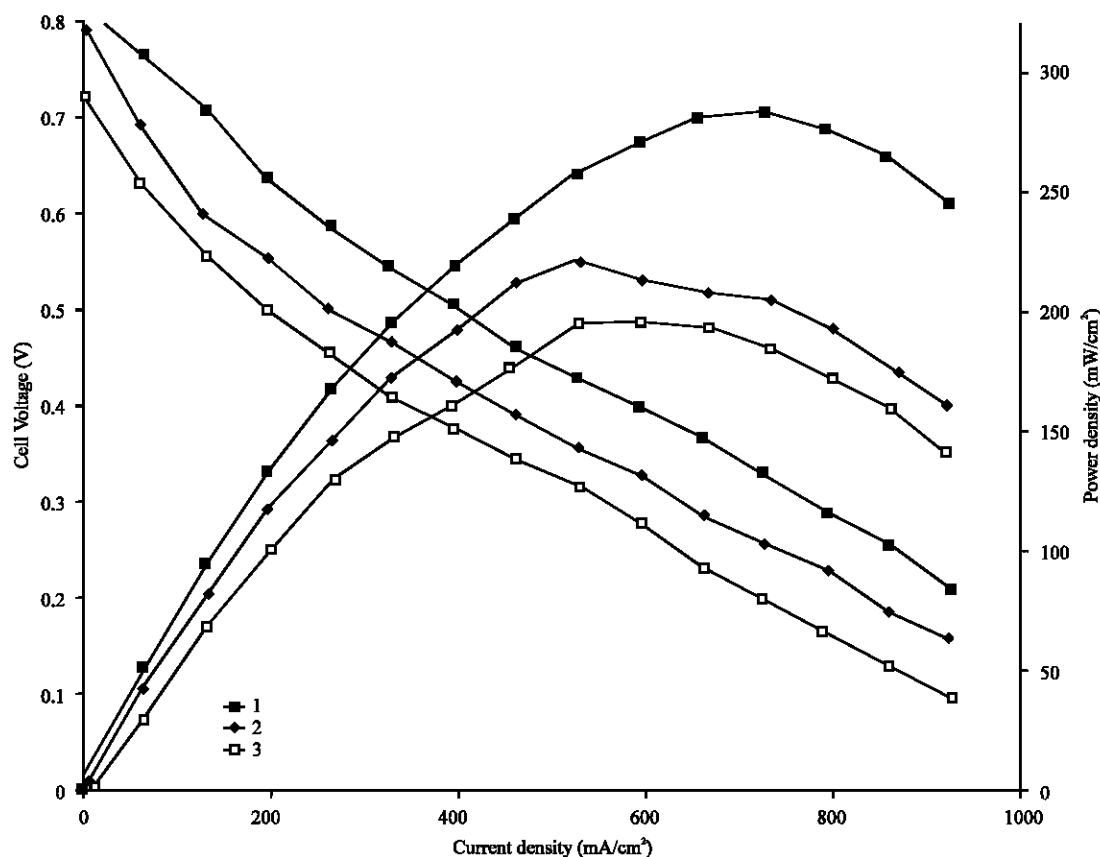


Fig. 2: Polarization and power density curves of AMFCs with PS-PFPP/SiO₂; 1) PS-PFPP/CNT; 2) Composite membranes and pure PS-PFPP and 3) Membrane at 60°C

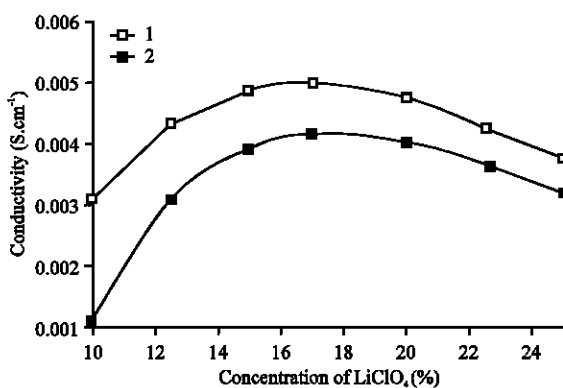


Fig. 3: Influence of lithium perchlorate concentration and polymer viscosity on electrical conductivity of SPE; 1) 0.32 dL.g⁻¹ and 2) 0.45 dL.g⁻¹

particles are uniformly distributed over the investigated surface. The mean particle size is about 20-30 nm. The most interesting notice is the adsorbed polymer films enveloping LiClO₄ particles as a fur coat. These films form a continuous network which according to our suggestion promote the SPE ion conductivity.

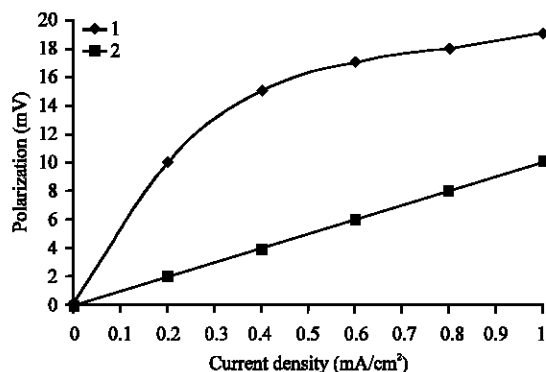


Fig. 4: Change of lithium polarization during charge-discharge cycling in Li-SPE-Li system: 1) 1st cycle; 2) 50th cycle

The given data suggest that the properties of PS-based SPE are stable in cycling process alongside with lithium electrode polarization reduction. To explain this high stability, we suggest that the surface of lithium electrode doesn't undergo the significant changes during charge-discharge process. To check this assumption the lithium electrode surface was investigated by electron

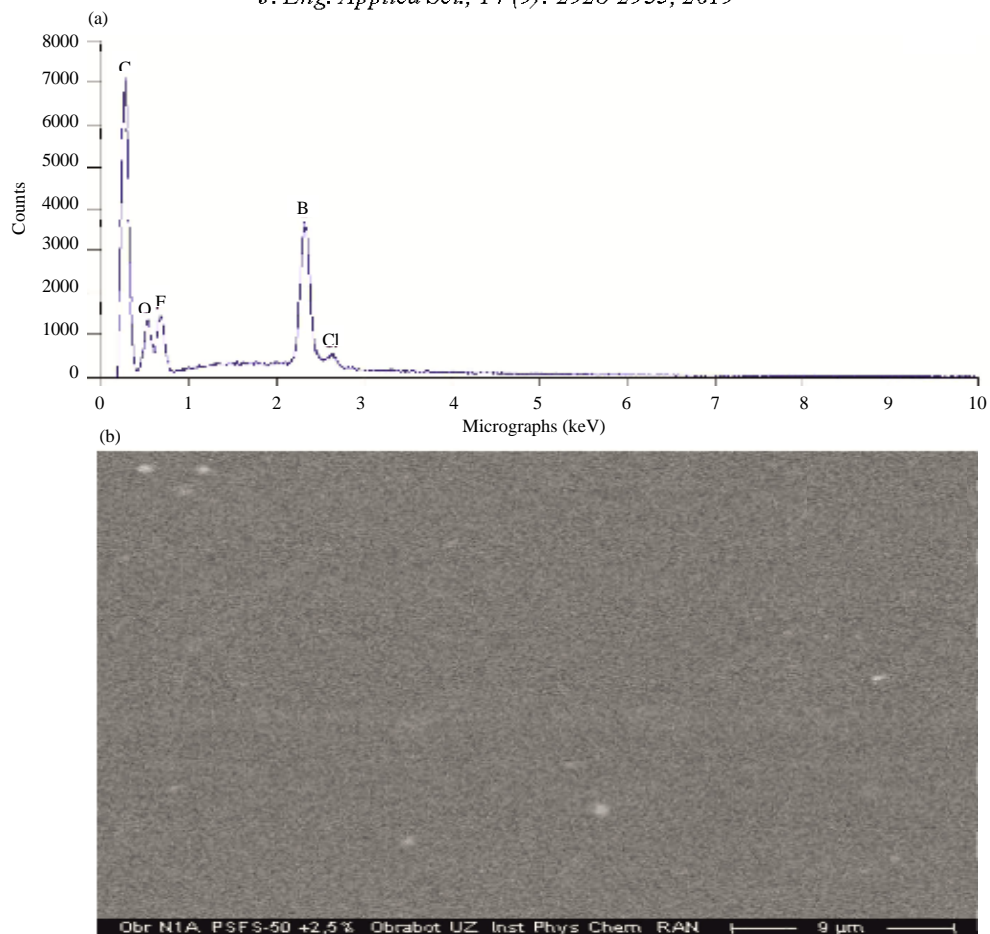


Fig. 5: Elemental composition obtained using XEDS; a) And SEM micrographs and b) Of PS-PFPP-based SPE with 1 M LiClO₄ solution

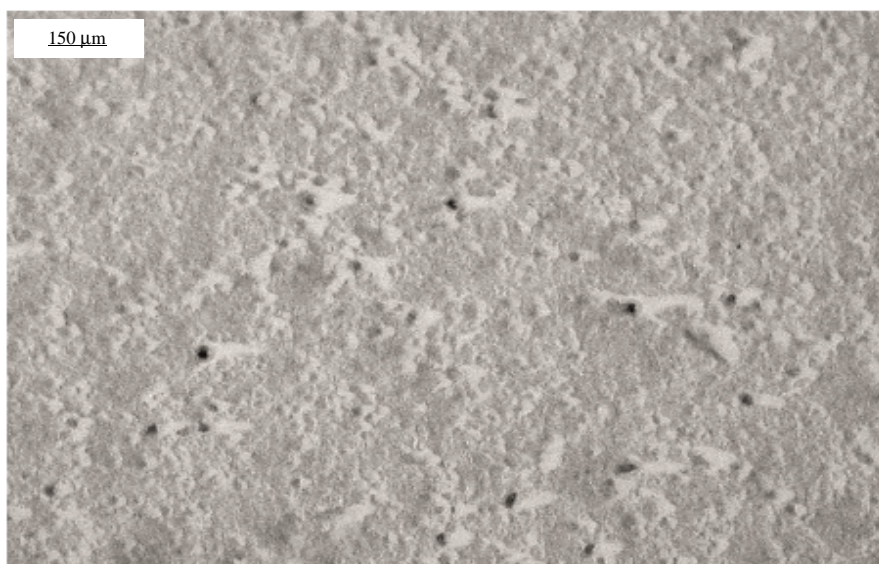


Fig. 6: TEM micrographs of PS-PFPP-based SPE with 1 M LiClO₄ solution

microscopy after 1 and 100 charge-discharge cycles in Li-SPE-Li cell. The results showed that initially the lithium electrode surface there are only acicular particles. During charge-discharge process the scaly form particles are generated on electrode surface alongside with acicular particles. In general, the lithium electrode surface becomes more homogeneous in comparison with the initial surface. It should be noted that the dendrite-formation centers on lithium surface are completely absent. SPE described above were used during Li-LiV₃O₈ and Li-LiFePO₄ batteries testing (Smirnov *et al.*, 2010; Vorob'ev *et al.*, 2015) which have confirmed its applicability in Li-ion batteries. Results obtained in presented research show that the conductivity of PS-PFPP-based SPE surpasses the conductivity of possible alternatives. Very important result is that PS-PFPP-based SPE almost doesn't interact with the anode which suggests very high persistence of the lithium power source with PS-PFPP-based SPE.

CONCLUSION

At present research novel PS-PFPP-based SPEs and membranes doped by SiO₂ and CNT were studied. AMFC composite membrane modified by SiO₂ demonstrated better electrochemical performance at 25-60°C during alkaline fuel cell testing compare to pure and CNT modified ones. Thus, a new opportunity of effective materials developed for AMFC. Moreover, SPE based on PS-PFPP copolymer showed high electrical conductivity, good adhesion to electrodes, high mechanical strength, stability and inert behavior towards other battery components. It can be used in Li-ion batteries for different application, for example, energy and utilities, portable devices, communication systems, etc.

ACKNOWLEDGEMENT

The study was carried out under State assignment No.13.2052.2017/PCh of the Ministry of Education and Science of the Russian Federation.

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