Ion-exchange membranes for low-temperature fuel cells

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Introduction

Energy from fuel cells has been recognized for tens of years as one of the most perspective alternative source of energy. The fuel cell is a device that through chemical reactions produces energy. The only products of these reactions, except the energy, are heat and water. Fuel cells are highly efficient, environmentally clean (there are no harmful reactions products) and have high energy density. Conversion of the chemical energy into electrical energy can occur continuously, as long as enough fuel is supplied [1].

The first, working fuel cell was constructed by William Graves, Welsh scientist in 1939, based on the publication by Friedrich Schönbein, Swiss chemist. The paper described principles of hydrogen-fueled cell operation[2]. This attracted great interest, but due to the difficult times and II World War, research on that topic was not continued and fuel cells were not developed, not until the 1960s, when "the conquest of space" has begun . New ways of transportation and power supply for spacecraft were in high demand – it enabled rediscovery of fuel cells. The exploration of their practical use has begun, fuel cells were subjected to intensive studies, what allowed for their continuous development. Satisfactory results of research projects enabled the practical use of alkaline fuel cells for spacecraft, including Apollo and the deployment of such cells as power sources for space stations. Fuel cells created by teams of American scientists provided heating and electricity for astronauts during their expeditions, as well as continuous access to water by condensation of by-products (namely water vapor) of fuel cell reactions [3].

Fuel cells are becoming more and more desirable energy source, especially in times of energy crisis. In the era of depleting fossil fuels, fuel cells play prominent role among the innovative solutions for energy production. High efficiency, quality of produced energy as well as no harmful by-products allow to apply fuel cells in hybrid systems for automotive purposes, as well as supply for medical equipment, computers, etc. [4].

Every fuel cell consists of few key components, most important of them being electrodes and electrolyte. Electrolyte in fuel cells plays three main roles: ion conductor, electron insulator and separator – it is key component of fuel cells. The importance of electrolyte can be seen, that one of the main ways to divide fuel cells is based on type of electrolyte used. Moreover, the electrolyte determines type of fuel that can be used and defines working range of temperature of such cell [5].

Most of modern fuel cells are based on functionalized polymer membranes, which play role both of separator and electrolyte. Suitably modified membrane can conduct hydroxyl and hydronium ions depending on introduced active groups. Solid electrolyte can replace liquid electrolytes, i.e. strong acids and bases. Elimination of aggressive compounds from fuel cells shall increase lifetime of fuel cell components and, what is even more important, decreases their impact on environment and ensures their safe usage [6].

Research is nowadays mainly focused on seeking cheap and durable membranes that could operate in wide range of temperatures, as well as cheap catalysts that increase efficiency of new solid polymer electrolytes. Most of the studies pursue creation of proton-exchange polymer membrane. Despite their excellent chemical and mechanical properties, high thermal stability and acceptable ion conductivity, there are still serious drawbacks preventing fuel cells from becoming commercially available. Main disadvantages of fuel cells with proton-exchange membrane are following: expensive catalysts poisoning with carbon monoxide (by-product in some of the fuel cells, high fuel permeability that contributes to the system contamination and slow kinetic at the electrode/electrolyte interface [7÷9]. Those are the reasons behind higher and higher popularity of research concerning fuel cells with anion-exchange membranes. Obviously faster kinetic of oxygen reduction kinetics in alkaline environment allows to increase kinetic of all fuel-cell reactions. Moreover, fuel anode reactions occurring in methanol-fueled cells are faster in that case, as alkaline environment facilities their progress. Besides, alkaline anion-exchange membranes can use cheaper catalysts, containing more common metals like nickel or silver in comparison with platinum-based catalysts usually used in cells with proton-exchange membrane. Research concerning alkaline anion-exchange membranes usually searches for possibilities to obtain membranes based on polystyrene or polysulfone resins which are characterized by high thermal and chemical stability, as well as low market price. [10÷12]. In the last years possibilities of application of another anion-exchange membrane material are being studied – other ion-selective polymers, such as polyetherimides are taken into consideration. Papers concerning use of polyetherimides as polymer matrices for alkaline anion-exchange membranes have appeared recently [7, 13÷15]. The main objective of the current publication was to produce anion-exchange alkaline membrane using tin (II) chloride as the reaction catalysts. Second objective was to study possibilities of its application as a solid-state membrane in fuel cells.

Experimental Section

Details of the anion-exchange membrane synthesis

Ion-selective polymer membrane, capable of hydroxyl anions transportation was synthesized in three-step reaction. The polymer, polyetherimide was subsequently chloromethyled, quaternized and alkalized (Fig. 1). The established method for membrane synthesis was applied [7]. A new idea was to use a different catalyst for chloromethylation reaction, i.e. tin (II) chloride.

During the first step, 2 g of polyetherimide (PEI, Aldrich) were dissolved in 15 ml of 1,2-dichloroethane (CH_2ClCH_2Cl, analytically pure, Chempur) with tin chloride ($SnCl_2$, >99.9%, Aldrich; 5% of polymer mass). The mixture was continuously heated to maintain the temperature reaction (80°C). Upon complete dissolution of polymer (after approx. 2h) 1.3 ml of chloromethyl methyl ether was added in portions (CH_3OCH_2Cl, technically pure, Aldrich). Then the system was subjected to continuous, prolonged mixing.

The product obtained in the first step of the process was alternately rinsed with methanol and double-distilled water in order to remove solvent, catalyst and by-products residues and subsequently dried under vacuum at 70°C.

In the second step of the process polyetherimide with introduced chloromethyl groups was dissolved in N,N – dimethyloformamide

(C$_3$H$_7$NO, analytically pure, Chempur). The mixture was then pour into Petri dish and dried for 18h at 85°C. Obtained transparent polymer membrane (Fig. 1) was in the next step quaternized by immersion in 30% trimethyloamine solution (N(CH$_3$)$_3$, analytically pure, Aldrich). Quaternization reaction was carried out in 14h at 30°C.

Subsequently membrane was rinsed with double-distilled water to remove solvent and dried under vacuum at room temperature, During last stage of the process polyetherimide membrane with amine groups introduced into chain was treated with 1 mol potassium hydroxide aqueous solution (KOH, analytically pure, Chempur) at room temperature for 24 hours. After finishing the last process membrane was rinsed several times with double-distilled water. The membrane, prepared in such a way, was subjected to further testing.
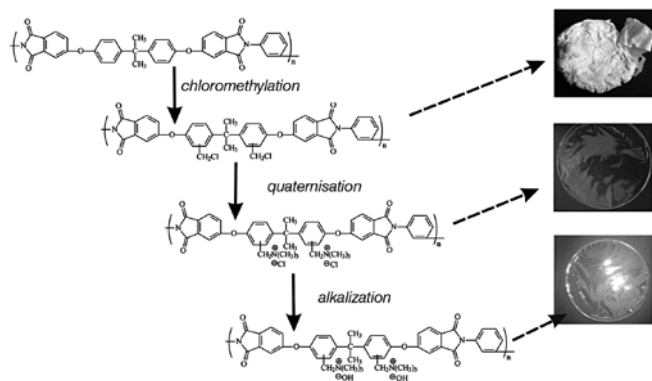

Fig. 1. The scheme of the three-step production method of anion-exchange polymer membrane

Physical and electrochemical properties of anion-exchange polymer membrane

Products obtained during each step of synthesis of anion-exchange polymer membrane was photographed (Fig. 1) after removal of solvents and drying in vacuum dryer.

The structure of dried alkaline ion-exchange membrane was analyzed topographically using Scanning Electron Microscopy (SEM). ZEISS EVO®40 scanning electron microscope was used to obtain topographic characteristics of the membrane.

Studies of thermal decomposition of alkaline ion-exchange membrane were carried out using thermogravimetric method for pure polyetherimide, as well as process intermediates: chloromethylated and quaternized polyetherimide and final product – alkaline anion-exchange membrane. Measurements were carried in argon atmosphere in temperature range 50–900°C, while heating rate was 10°C/min. Measurements were carried out using Netzch STA 409C 3F differential thermal analyzer.

In order to study membrane absorbing capacity, fragments of the thoroughly dried polymer membranes of known weight were prepared. They were immersed in containers with distilled water. The changes of polymer membrane's weight were measured for different time durations. Amount of absorbed solvent has been indirectly determined by analysis of weight changes of particular samples and calculated in the following way:

$$\text{increase of membrane's weight} = (m_t\text{-}m_0/m_0)*100\%$$

where: m_0 – mass of dry membrane, m_t – mass of membrane after given time.

Specific conductance of alkaline anion-exchange membrane was measured using two-electrode Swagelok® system, where between two platinum electrodes the polymer membrane in form of discs of known diameter and thickness was placed. Membrane discs

prior to measurement were placed in 1 mol/dm³ aqueous solution of potassium hydroxide for 12 hours and subsequently flushed and placed in double-distilled water for another 12 hours. Membrane samples were prepared in room temperature. Immediately before the measurement they were dried and placed in measuring cell. PARSTAT 2266 device and Vötsch environmental chamber, allowing to control measurement temperature with precision up to ±0.2°C. The measurements were carried out in the range of 20–100°C. Conductivity was calculated from Nyquist plot.

Results and Discussion

As mentioned before, the synthesis of alkaline anion-exchange membrane is a three-step process. The first step of synthesis, i.e. chloromethylation of polyether, allows to modify chemically the polymer chain by introducing active chloromethyl groups. This step determines quality and yield of the entire process [13]. Number of chloromethyl groups introduced in polyetherimide chain determines directly the number of hydroxyl groups that can be introduced in the last step of synthesis, i.e. alkalisation. While number of the OH⁻ groups introduced in the polymer chain influences directly ionic conductivity, i.e. one of the most important electrochemical parameters of ion selective membranes used in fuel cells. Temperature stability and reaction time have been established as parameters determining quality of obtained polymer membrane. Moreover, it has been observed that when tin chloride is used as a catalyst, the step of chloromethyl addition to polyetherimide chain might be carried in slightly higher temperatures than for other types of catalysts [13, 15]. Furthermore, the amount of catalyst as high as 5% of polymer mass might be added without causing gelation of the system at 80°C.

During chloromethylation, when active aromatic rings are alkylated with chloromethyl groups, uncontrolled internal cross-linking may occur due to the Friedel-Crafts reaction. This has a negative effect on amount of introduced chloromethyl groups.

Topographic analysis of ion-selective alkaline membrane has shown the alkaline anion-exchange membrane surface and cross-section (photo 1).
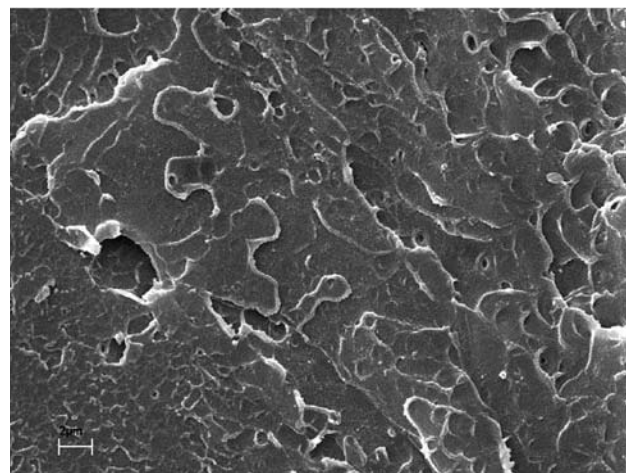

Photo 1. Scanning electron microscopy image of anion-exchange membrane surface.

Some surface irregularities (cavities of approx. 8 μm diameter) have been observed. They should not cause any additional internal resistance when membrane is used in the measurement systems, but the further improvement of membrane manufacturing technology might be necessary in order to remove all surface defects.

Additionally, thermogravimetric measurements were performed (Fig. 2) for pure polyetherimide (PEI) and for modified polymers after subsequent steps of synthesis: chlorated (PEI-CH2Cl), quaternised (PEI-TMA) and alkalized polymer (PEI-OH).
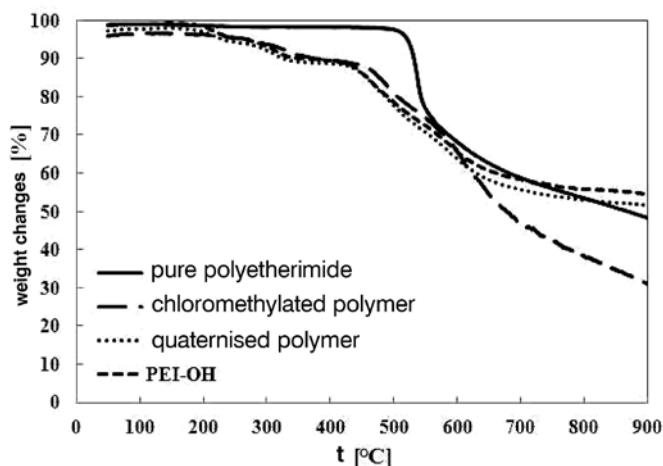
Fig. 2. Thermogravimetric analysis of polymer material in form of alkaline anion-exchange membrane (PEI-OH) and products of subsequent synthesis steps:

All polymers were stable thermally in 50–450°C temperature range, what suggests they might be used as working electrolytes for fuel cell production.
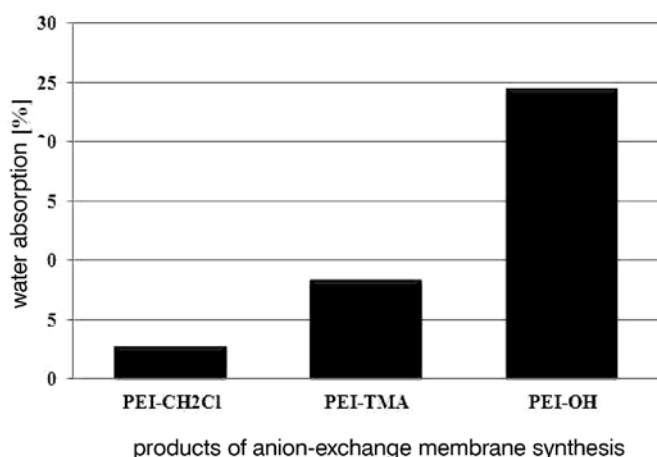

products of anion-exchange membrane synthesis

Fig. 3. Absorption capacity of polymer membrane and products of subsequent steps of synthesis (PEI-CH2Cl – product after chloromethylation , PEI-TMA – product after polymer quaternisation)

Highest absorption capacity for distilled water (Fig. 3) is shown by PEI-OH alkalized anion-exchange membrane (24.89%) followed by the PEI-TMA, quaternized polymer membrane (6.78%) and PEI-CH2Cl polymer chain chloromethylation product (3.65%). So large differences in absorption capacity for water molecules of products of particular steps of the membrane synthesis are caused by the different structure of the substituents. Polyetherimide with introduced hydroxyl groups has highest polarity, what causes increased absorption of polar water molecules and this material has highest hydrophilicity.

Figure 4 shows effect of temperature on specific conductance of alkaline anion-exchange membrane. The conductance increases significantly with temperature in the 20–60°C range. Above 60°C degrees the increase is much less pronounced – conductance has a value in the range $2.12 \times 10^{-3} – 2.23 \times 10^{-3}$ S/cm. After disassembly of fuel cell anion-exchange membrane has shown no signs of wear, damage or deformation. Based on conducted studies it might be stated that conductance of alkaline anion-exchange membrane increases with temperature and its structure is stable at 100°C. This confirms possibility of alkalized poliamide membranes application as electrolytes in fuel cells [7, 10].
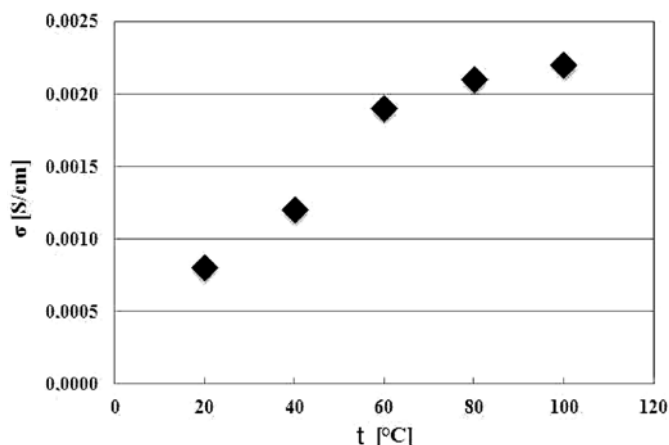

Fig. 4. Effect of temperature on specific conductance of alkaline anion-exchange membrane in the temperature range of 20-100°C

Summary

The anion-exchange polymer membrane production method from poliotheroimid polymer matrix with tin (II) chloride as a catalyst for chloromethylation reaction. The use of tin (II) chloride as a catalyst during alkylation of polymer chain allowed to perform the reaction at 80°C temperature in 10 h with no gelation effect that occurs due to side reactions that cause polymer cross-linking. This in turn negatively affects number of chloromethyl groups introduced to polymer main chain and effectively decreases amount of hydroxyl ions in polymer. Alkalized ion-exchange membrane has high water absorbance capacity.

Specific conductance of alkalized polyethereimide membrane increases with the temperature. In the range of temperatures 20-100°C the membrane is highly stable, while conductance is $2.12\text{-}2.32 \times 10^{-3}$ S/m. The stability of the anion-exchange polymer membrane with hydroxyl groups has been also confirmed using thermogravimetric methods – it is stable in the 50-450°C temperature range, which means that it can be applied as an electrolyte in fuel cells.

Acknowledgments

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Like water for batteries

Objects made from graphite, such as lithium-ion batteries, are „hydrophobic". For decades this has presented significant challenges in terms of building more durable technological devices made with graphite.

It appears that past samples of graphite were likely contaminated by air, causing the samples to appear hydrophobic, according to a University of Pittsburgh study. The Pitt team has demonstrated (for the first time) that these materials are actually intrinsically attracted to water (hydrophilic). The findings have particular implications for lithium-ion batteries and super capacitors, as both battery types are built from these materials. These findings may hold implications for producing stronger, more durable batteries.

The team found that, when graphite and graphene are exposed to air, a thin layer of hydrocarbon (a compound made entirely of hydrogen and carbon) quickly contaminated the surface. Using infrared spectroscopy and X-ray photoelectron spectroscopy, the team was able to see this hydrocarbon layer, noting its hydrophobic nature. However, when the team used heat to remove this contaminant layer, the surface became hydrophilic.

(Source: http://www.chemistrytimes.com/research/Like_water_for_batteries.asp, 12.08.2013)

Materials break, then remake, bonds to build strength

Scientists could one day use the stress-induced strength from these new materials to make better fluids such as engine oil, or soft-structure substances such as artificial heart valves. Materials like this wear out over time because of the repeated mechanical forces they experience during use. But if a material had properties to slow down its destruction, it would greatly improve quality of life. It is the first time scientists have used force-induced chemistry within a material to make it stronger in response to stress.

In past experiments, Steve Craig and his team has gripped and tugged on individual molecules of a material to see how it reacted at the atomic level. Now, the scientists have scaled up the material to contort it macroscopically and see how it responds. The response is similar to what happens when a person lifts weights. Those individual stresses trigger biological processes in the muscles that ultimately increase the person's strength.

The new man-made materials have characteristics already in place so that when a stress triggers a bond to break, it breaks in a way that triggers a subsequent reaction forcing the busted atomic bonds to reform new ones.

One drawback to the new materials is that forces deform the material's initial structure. It is stronger at the end, but is not the same shape. The team now plans to create synthetic materials that can repair themselves after stress and retain their original shape.

(Source: http://www.chemistrytimes.com/research/Materials_break_then_ remake_bonds_to_build_strength.asp, 20.08.2013)