RESEARCH OF PROTON CONDUCTIVITY OF GRAPHEN-GRAPHAN CONTAINING MEMBRANES

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Introduction

The compositions with essential conductivity and thermostability in the 180-500 °C temperature range among known protonconductive materials are absent [1, 2]. The creation of the materials with thermostability and high proton conductivity in mentioned temperature range is the actual problem. This problem's solution would allow suggesting the new ionselective membranes for the middle temperature fuel elements and the membranes catalysts of the acid-basic type for the processes of the oil processing and petrochemistry as well.

Results and Discussion

The β-alumina, the proton decationative zeolites of the X and Y type are possessed of own proton conductivity (though not high) under the temperatures exceeding 300 °C. The most established high temperature conductors with the perovskite's structure are possessed of the essential proton conductivity (to 10^{-3} S/cm) only in the 500-800 °C temperature range and in the moist medium or in the hydrogen atmosphere. By the protons' transport mechanism the graphen-graphan containing materials [3] (for example being got by the oxidative acetylene's polymerization [4,5]) are the most similar to the perovskite structure. In the similar systems like to the perovskites the protons are formed on the crystallites' surface or it are generated from without and then are injected into the crystalline lattice or into the polymer's circuitry with the system of the conjugated (twinned) carbon-carbon's bonds. The last, as it is known, is the good conductors of the electrons. However, under the conditions if the electrons' transfer into the polymer's structure is blocked and if the protons from the independent source are injected simultaneously as well, the protons' transport becomes possible along the system of the multiple bonds [6].

The aim of the presented work is the research of the injected proton conductivity of the polyconjugated polymers in the hydrogen atmosphere under the 50-500 °C temperature range.

The product of the acetylene's oxidative dehydropolycondensation (PA) (which had been synthesized according to the method [5]), the product of the carbamide's homopolycondensation (PCA) (which had been synthesized as to the method [7] under the 480 °C and 7,0 MPa pressure), the product of the C-70 polyvinilchloride's dehydrochlorination in the inert medium under the 200-460 °C (PVC) as the classical electroconducting polymers have been chosen as objects of the investigating. The synthesized powder-like materials are insoluble in the organic solvents and are stable in the inert and reducing medium till 500 °C. The membranes on the base of the synthesized polymers were obtained by it's plotting on the porous elastic base. In the capacity of the last the thermostable fabric "Kevlar" type (production of the Dupon Company) has been chosen.

The control over the structure of the synthesized polymers has been carried out by the Fourier IR-spectroscopy method. The IR-specters have been measured on the spectrophotometer Nicolette 320X FTIR in the 4600-420 cm^{-1} frequencies range. The analysis of the Fourier IR-specters of the synthesized materials have demonstrated the availability of the linear hydrocarbon fragments with double, triplicate, with coupled double and triplicate or twinned double bonds between carbon atoms, carbon and nitrogen atoms in its molecules. The product of the polyvinylchloride's dehydrochloration (PVC) differ by the aromatic rings' presence in the structure as well.

The proton conductivity of the materials in the 20-500 °C temperature range have been determinated on the designed laboratory installation under the constant 10 V difference of the potentials on the electrodes.

For the comparison during the measurements' carrying out the electrodes of two types have been used: the active for the splitting of the hydrogen – on the base of the fine-dispersed nickel (being obtained by the nickel's reduction from its nitrate salts by the hydrogen's stream under the 320 - 500 °C) and inactive for the hydrogen's splitting (protonblocking) – on the base of the sintered aluminium.

The use of the blocking aluminium electrodes excepts the stage of the protons' generation on the electrode's surface. The obtained meanings of the specific conductivity (æ) of the researching membranes characterize its electron conductivity (which is rising with the temperature) in this case. In the temperature range 200-500 °C the electron conductivity of the materials changes from $8{,}6 \cdot 10^{-12}$ to $3{,}8 \cdot 10^{-8}$ S/cm (table 1), which is corresponds with literature data of the electroconductivity of the polymer semiconductors.

Table 1. The specific conductivity (æ, S/cm) of the membranes on the base of the synthesized materials in the hydrogen atmosphere.

Tempe-rature, °C	Elec-trode	The specific conductivity (**æ,** S/cm) of the membranes		
		PA	PCA	PVC
200	Ni	$3{,}0\ 10^{-5}$	$3{,}5 \cdot 10^{-5}$	$8{,}0 \cdot 10^{-6}$
	Al	$8{,}6 \cdot 10^{-12}$	$5{,}2 \cdot 10^{-10}$	$6{,}8 \cdot 10^{-11}$
300	Ni	$4{,}0 \cdot 10^{-5}$	$5{,}7 \cdot 10^{-5}$	$1{,}5 \cdot 10^{-5}$
	Al	$1{,}0 \cdot 10^{-11}$	$1{,}9 \cdot 10^{-9}$	$8{,}2 \cdot 10^{-11}$
460	Ni	$4{,}1 \cdot 10^{-3}$	$1{,}05 \cdot 10^{-4}$	$4{,}5 \cdot 10^{-5}$
	Al	$3{,}6 \cdot 10^{-10}$	$3{,}8 \cdot 10^{-8}$	$6{,}5 \cdot 10^{-10}$

The meanings of the specific conductivity of the investigating membranes with the use of the active nickel's electrodes are raised on the 5-6 degrees and amount to $8{,}0 \cdot 10^{-6} - 4{,}1 \cdot 10^{-3}$ S/cm. In this case the total specific conductivity of materials is defined by its proton conductivity. The contribution of the electron constituent is not exceeded 0,001 %, moreover the smallest one ($1 \cdot 10^{-5}$ %) is for the membranes on the base of the product of the acetylene's dehydropolycondensation(PA).With temperature increase from 200 to 460 °C the meanings of the proton conductivity of materials are raised on the 1-2 degrees – to $4{,}5 \cdot 10^{-5} - 4{,}1 \cdot 10^{-3}$ S/cm. The lowest proton conductivity has been demonstrated by the material based on the product of the polyvinylchloride dehydrochloration (PVC), which structure contains condensed aromatic rings besides the linear groupings with the couple multiple bonds.

As mentioned above the researching materials in its structure do not contain the ionogenic groups which are capable of the protons' generation and do not possess of the own proton conductivity. On the assumption of the proton generation on the nickel electrode and its injection into the membrane the last is capable to transportation of protons to the second electrode and thus to ensure the proton conductivity of the membrane which rises with temperature.

In our opinion the transport of the injected protons in the researching materials is realized along the chains of the couple and twinned multiple bonds.

Conclusions

Thus, in this work there are suggested the high temperature graphen-graphan containing protonconductive materials, which do not contain the ionogenic groups in its structure, but contain the system of the couple and twinned multiple bonds and in the medium of hydrogen possess the injected proton conductivity in the wide temperature range of 50-500 °C.

References

1. Alberti G., Casciola M. Solid state protonic conductors, present main applications and future prospects. Solid State Ionics. 2001; 145: 3-16.
2. Pat. 2002031695 US, МПК H01B1/12; H01M8/02; H01M8/06; H01M8/12; H01B1/12; H01M8/02; H01M8/06; H01M8/12 Hydrogen permeable membrane for use in fuel cells and partial reformate fuel cells system having reforming catalysts in the anode fuel cells compartment / Smotkin E.S. – Publ. 14.03.2002.
3. Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A. Electric field effect in atomically thin carbon films. Science. 2004; 306(5696): 666 – 669.
4. Handbook of Organic Conductive Molecules and Polymers, Conductive Polymers: Synthesis and Electrical Properties / By Hari Singh Nalwa**,** Vol .2. – New York: J. Wiley & Sons, 1997. – 888 p.
5. Коршак В.В., Сладков А.М., Кудрявцев Ю.П. Синтез полимерных ацетиленидов. Высокомолекулярные соединения. 1960; 2(12): 1824-1827.
6. Запороцкова И.В., Лебедев Н.Г., Запороцков П.А. Протонная проводимость однослойных углеродных нанотрубок. Физика твердого тела. 2006; 48(4): 756-760.
7. Паушкин Я.М., Лунин А.Ф., Омаров О.Ю. Полимеры с сопряженными связями из углекислого и двууглекислого аммония. Высокомолекулярные соединения. 1964; 6(4): 734-736.