Agar as a compound of alkaline solid polymer electrolyte

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Abstract: The paper presents results of a study on the possibility of using the method of physical cross-linking for production of hydrogel alkaline electrolytes, using poly(vinyl alcohol) (PVA), agar (AG) as a gelating medium and potassium hydroxide (KOH). The optimum composition of reaction mixture and optimum procedure for production of polymer electrolytes in the form of membranes using biodegradable oligomer agar showing gelating properties were established. Detail physicochemical characterization, including assessment of thermal stability of hydrogels, their ability to absorb water phase and the possibility of ions transportation was performed. The attempts at using agar as a gelating medium and a biodegradable component of gel alkaline electrolytes have opened new perspectives for the use of these compounds are safe and environmentally friendly components of fuel cells containing alkaline water electrolytes. In order to confirm and characterize the performance of cells containing alkaline polymer electrolytes with addition of agar as a gelating agent, model elastic nickel-hydride batteries in pouch type construction, containing polymer electrolytes of optimum parameter were made and tested in defined conditions and under certain loading.

Key-Words: - polymer electrolyte, Ni-MH, agar, battery, PVA, alkaline polymer electrolyte, Nickel-metal Hydride battery

1 Introduction

Liquid electrolytes commonly used in chemical current sources are characterized by relatively high ionic conductivity but the gravimetric energy density produced by the cells with liquid electrolyte is much lower than that of the cells with polymer electrolytes. Moreover, in the case of failure, volatile vapors of organic solvents contained in the electrolyte can initiate explosion and thus to combustion of the cells, which is a frequent problem when working with lithium-ion cells (Li-ion). It seems that a good solution is the use of polymer electrolytes. All over the world the search for safe and effective technologies for production of polymer solid state electrolytes is continued. Such electrolytes devoid of liquid phase would be much safer in use and would have the same of improved parameters of work as the liquid ones. Moreover, polymer electrolytes would act as separators and would be responsible for ions transportation. A concept which is a compromise between the cells with liquid and solid electrolytes employs the gel polymer electrolytes in which a liquid phase still exists but in much limited amount. At present the top issue is to find solutions for lithium -polymer batteries however, however, all the time much effort is devoted to solid state electrolytes for alkaline batteries in which water solvents have been used [1-6].

Although at present the market is dominated by lithium cells, the relatively high cost of their production, depleting lithium resources and no guarantee of work safety, they are far from ideal solutions for energy storage and conversion. Much cheaper and much safer in use seem to be nickel-hydride (Ni-MH) cells with a solid state or gel electrolyte. Traditional Ni-MH cells are characterized by low cost of production, availability of components, high reliability and safety of work and relatively easy way of utilization. However, their technology based on liquid electrolytes is marred with a few drawbacks (like low potential, memory effect) that decided about phasing out Ni-MH batteries from the market by li-ion ones [7-9]. Alkaline polymer electrolyte, in contrast to the conventional alkaline water electrolyte of potassium hydroxide (KOH) in Ni-MH batteries could contribute to saving many problems, e.g. electrolyte leakage, oxidation of the negative electrode (the hydrogen-storing alloy) after the cycle of work, which can decrease the memory effect and self-discharge of the battery. Moreover, reduction of the battery weight by elimination of hard case and replacing it by flexible and soft case, would increase safety of work and increase the energy density in the battery [10-11].

As follows from literature, alkaline polymer electrolytes have been made mainly with polyethylene oxide (PEO) or polyvinyl alcohol (PVA) as matrices of alkaline polymer electrolytes. It has been established that the electric conductivity of alkaline polymer electrolytes based on PVA is usually higher than that of the PEO-based electrolytes, and reaches values of the order 10-2 Scm-1. Unfortunately, PVA-based electrolytes easily undergo dehydration, which can lead to the loss of flexibility, breaking of the conducting membrane and battery failure [12-16]. Interesting additives to the polymer matrix of the electrolyte seem to be the compounds showing gelating properties that permit capturing much more amount of the liquid phase in the electrolyte structure, which leads to increase in the conductivity and flexibility of the system [17-19]. Agar-agar known as agar (AG) is a natural chemical compounds from the group of polysaccharides, of high molecular mass and very good gelating properties. It is often used as a gelating component in food industry, described by the symbol E406. Agar-agar in cold water swells, is well water soluble at 90-100°C, while it forms gel at 40-50°C. The solidified gel dissolves upon heating to 90-100°C [20].

The aim of the study presented was to obtain alkaline polymer electrolytes by the method of physical cross-linking, using PVA, AG and KOH at different weight ratios, and comprehensive characterization of the electrolytes obtained, in view of their prospective use in elastic Ni-MH cells.

2 Experimental

A series of alkaline polymer electrolytes containing 0, 20, 30, 40 or 50%wt. of KOH with respect to the PVA/GG mixture were prepared. As a result of preliminary studies the optimum composition of the electrolyte of the highest stability was established as that of PVA to AG ratio of 1:3. The procedure for preparation of alkaline polymer electrolytes PVA/AG/KOH was as follows. A portion of 1.8g PVA (VWR, M_w 1150,00) was dissolved in 25 cm^3 of water and heated in water bath at about 90°C, upon continuous stirring. After 4h of vigorous stirring and heating, Agar (AG, Sigma-Aldrich) in the amount of 0.6g was added and then the system was shaken at a frequency from the range 350-380rpm, for 4h. The obtained solution PVA/AG after 24h was mixed with 15ml of water solution of potassium hydroxide (KOH, POCH) at certain weight ratios of 20:80, 30:70, 40:60 or 50:50, with respect to the KOH: PVA/AG mixture. Then, from the obtained solution showing high viscosity, air bubbles were removed by vacuum. The solution devoid of gas phase was poured onto a flat surface of a plastic mold and the process of physical cross-linking was started, in which the system was alternately frozen and defrosted in temperatures ranging from -20 to +20°C at the rate of 12^{o}C/min to complete 4 cycles. The thickness of the obtained hydrogel alkaline electrolytes in the form of membranes was in the range 0.02-0.062cm. Attempts were made at introducing KOH in the amounts greater than 50%wt. to PVA/AG matrix, but they failed because of the matrix disintegration so that the electrolyte was no longer in solid phase.

Topographic characterization of the electrolytes was made on the basis of scanning electron microscopy (SEM) images, permitting evaluation of the quality of the polymer electrolytes surfaces. SEM images were obtained on EVO®40 instrument made by ZEISS.

Thermal properties of the polymer electrolytes were evaluated on the basis of thermogravimetric measurements TGA, using an instrument STA 409C3F made by Netzsch. Measurements were made in the range 25°C - 600°C at the heating rate of 8°C/min in N_2 atmosphere.

The content of water in the hydrogel alkaline membrane was determined by measuring the changes in the membrane mass upon drying. Fragments of the hydrogel electrolytes of known mass were subjected to drying at 40°C in a moisture balance analyzer made by Radwag, until constant mass of the sample. The water content was the mass loss relative to the initial mass of the polymer electrolyte.

Measurements of conductivity of the alkaline polymer electrolytes were made by electrochemical impedance spectroscopy (EIS). The measuring system was a double electrode vessel of Swagelok type, in which a disc of the alkaline polymer electrolyte of known diameter and thickness was placed between two blocking electrodes of 1.27cm^2. The conductivity of the hydrogel electrolyte sample was read off from the Nyquist plot. Measurements were made at 25˚C, at frequencies from the range 0.1 Hz-100 kHz, at the potential amplitude of 0.01 V, using an instrument VMP SP-150 BioLogic.

For selected alkaline polymer electrolytes with addition of agar, the electrochemical stability window was determined and the performance of the electrolytes studied in elastic alkaline cells of pouch type was characterized. The tests were carried out in double-electrode systems of the type:

(-) 90% AB_5, 10%Ni | alkaline polymer electrolyte: PVA/AG/KOH | $Ni(OH)_2$/NiOOH (+)

Electrochemical stability of membranes was evaluated using cyclic voltamperometry (CV). Pieces of the alkaline polymer electrolytes studied were placed between two steel electrodes; the reference electrode was Hg/HgO. The tests were performed at 25°C in the potential window from -1.5 V to 1.5 V and scan rate of 20mV/s.

In the model pouch type battery made to test the performance of alkaline polymer electrolytes with agar, we applied special electrodes. The positive electrode was made of active filling for positive electrodes of the commercial name NICOL G extra heavy (Bochemie) and binding agent composed of 1.5% water solution of hydroxymethylcelullose (HPMC) and 55.6% suspension of polytetrafluoroethylene (PTFE). The active filling of the negative electrode was a mixture of powder-alloy reversibly adsorbing hydrogen, of AB_5 type (Auersrore IV: $MmNi_{3,55}Al_{0,3}Mn_{0,4}Co_{0,75}$) with 10% of carbonyl nickel and a binding agent of 3% PVA solution. The weighted portions of the active electrode fillings were pasted in the prismatic electrodes of nickel foam (Lyrun - China) of 1.6 mm in thickness and $500 g/m^2$ in density and pressed in a hydraulic press under 2 kN equivalent to about 5 MPa. The geometric area of the obtained electrodes was 6 cm^2. The electrodes were subjected to preliminary chemical activation in order to enhance the catalytic activity of the electrode alloy component in the reaction of hydrogen electrosorption in the cell. The chemical activation included etching of the electrode surfaces and removal of pollutants from their surfaces. The electrodes were immersed in 6M KOH of $d=1.25\pm0.01\ g/cm^3$ density for 24h. A similar procedure was applied for the separator of the cell with 6M KOH made of absorbing fibrous structure Viledon FS2119 (Freudenberg), which was the reference sample for the systems studied. The electrodes and the separator were activated for 24 h at 25°C, directly prior to the batteries assembly. After the activation, the excess of electrolyte was removed with a soft tissue from the surfaces of the electrodes and the separator. The system of two electrodes with hydrogel alkaline electrolyte of a known KOH content between them was placed in a polypropylene foil pocket.

The model nickel-hydride pouch type cells containing the alkaline polymer electrolytes of the highest conductivity and the reference pouch type cells with the typical commercial liquid electrolyte for Ni-MH cells, i.e. 6M of water KOH solution were subjected to a series of tests. The model batteries with alkaline polymer electrolytes were subjected to electric tests of galvanostatic cyclic charge/ discharge with C5/C5 currents expressed in terms of the active mass of the negative electrode. The battery was loaded and after 1h relaxation discharged to the potential of 1V.

3 Problem Solution

Exemplary SEM images of the surface of the polymer electrolytes composed of PVA, AG and KOH are presented in Fig.1. The porosity of the hydrogel structure definitely increased with increasing KOH content in the system. The size of pores is close to 2μm and the PVA/AG-KOH electrolyte structure is a kind of 3D lattice.

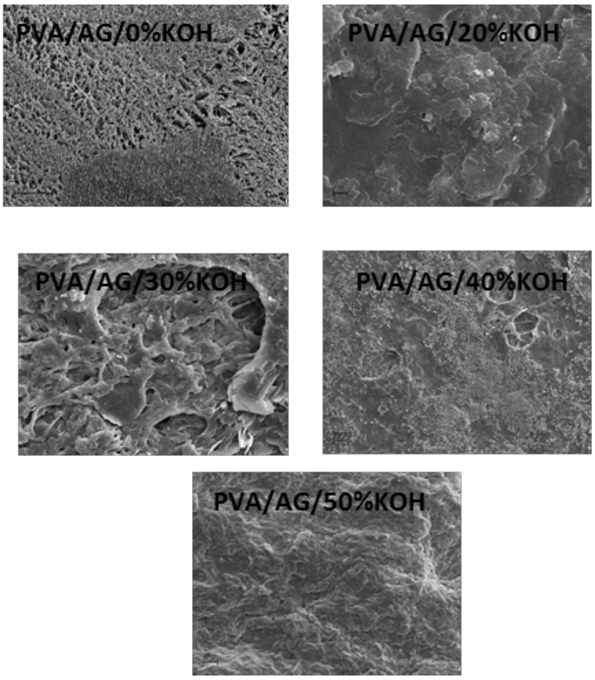

Fig.1 SEM images of a few PVA/AG/KOH polymer electrolytes.

As follows from the TGA measurements of the polymer electrolyte samples (Fig.2), their thermal stability decreased with increasing content of KOH in the ion-conducting membrane, although all the electrolyte samples were thermally stable in the range of work of a typical nickel-hydroxide electrochemical cell.

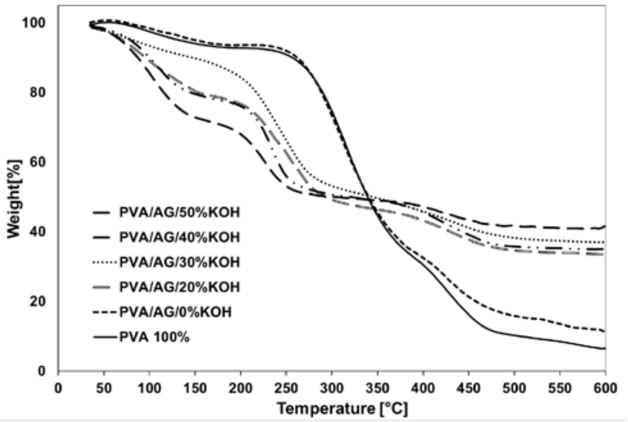

Fig.2. TGA curves recorded for all tested alkaline polymer electrolytes studied. As a reference sample the 100%PVA membrane was used.

The content of water in the alkaline hydrogel membrane was determined on the basis of the mass loss upon drying, as described in the Experimental 2. According to the results the content of water phase in the electrolytes containing 20-50%wt. of KOH relative to PVA/AG, reaches 78-80%wt. Only for the composite PVA/AG membrane without KOH, the water phase made over 90% wt. of all electrolyte sample.

We also made an attempt at evaluation of the regeneration abilities of the alkaline polymer electrolytes after total dehydration of the system. After immersion in distilled water of the alkaline polymer electrolytes totally devoid of liquid phase, after 3h the electrolyte samples recovered the physical and electrochemical properties of the original state (Fig.3).

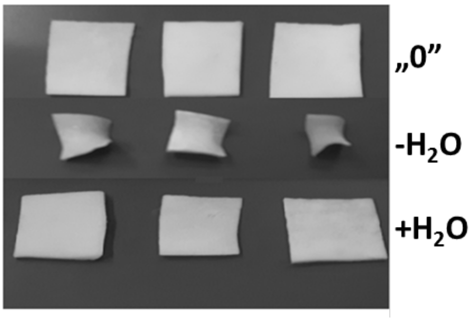

Fig.3. Regeneration process of PVA/AG/40%KOH: “0”- the initial state, -H_2O after dehydration and +H_2O after 3h in distilled water.

On the basis of electrochemical tests by EIS, the increase in conductivity of the samples was observed with increasing KOH content in the electrolyte. The highest conductivity was obtained in the system containing 50% KOH, e.g. at 25°C the conductivity of PVA/AG/50%KOH reached 0.24 Scm^{-1} (Fig.4).

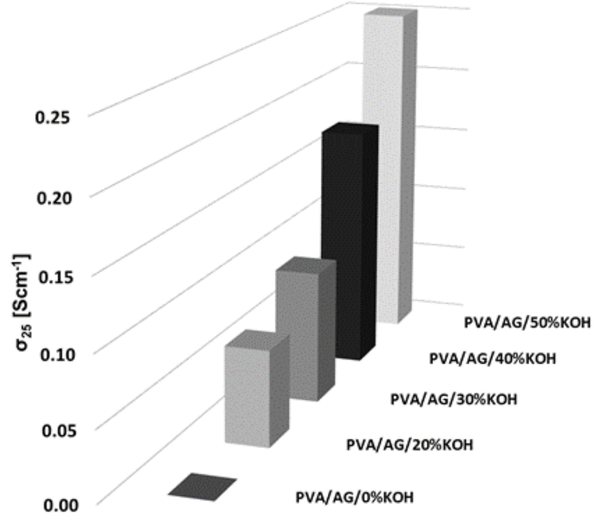

Fig.4. Comparison of conductivities of alkaline polymer electrolyte PVA/AG/KOH samples of different weight ratios of PVA/AG/KOH at 25°C.

Electrochemical stability windows were considered as one of the most important factors in practical applications of the alkaline polymer electrolytes PVA/AG/KOH, which were defined as a region of potential in which no considerable Faradic current flowed through the electrolyte. There were no significant difference in the electrochemical stability windows of the polymer electrolyte PVA/AG/KOH. Fig.5 presents the cyclic voltammograms for a one of tested alkaline polymer electrolyte. The electrochemical stability windows were ca. 1.43 V. Outside this range, the reduction and oxidation of the polymer electrolyte and OH^- ions could take place.

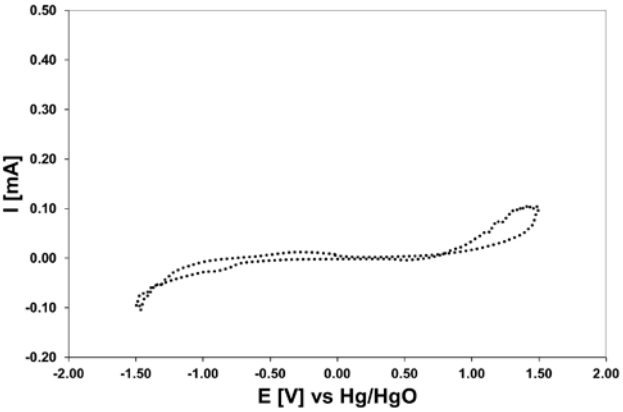

Fig.5. Cyclic voltammograph of the PVA/AG/50%KOH electrolyte.

The conductivity of alkaline polymer electrolytes PVA/AG/KOH were found to be lower than that for a 6M water solution of KOH which is typically used in Ni-MH batteries and whose conductivity at 25°C is 0.6 S/cm. However, in the aspects of safety of work and effectiveness of operation the alkaline polymer electrolytes with addition of agar are superior to liquid electrolyte (despite lower ion mobility) because of increase in gravimetric energy of the cell by elimination of heavy case and the possibility of adjustment of the cell shape to the instrument of device in which it is used and elimination of liquid phase which increases work safety.

On the basis of conductivity measurements, two alkaline polymer electrolytes with agar added showing the highest conductivity, were selected PVA/AG/40%KOH and PVA/AG/50%KOH. Conductivity value provides direct information on the transportation of ions in a given electrochemical system, so the other alkaline polymer electrolytes with addition of agar, showing lower conductivities, were rejected as not meeting the expectations. The Ni-MH cells were assembled as shown in Fig.6, using the electrodes prepared as described in the Experimental and the two alkaline polymer electrolytes with agar.

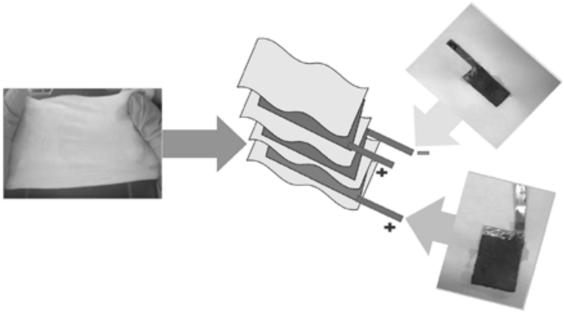

Fig.6. A scheme of assembly of an elastic Ni-MH cell of pouch type with alkaline polymer electrolyte.

An exemplary model Ni-MH cell of pouch type with PVA/AG/KOH electrolyte is presented in Fig. 7.

Fig.7. A model Ni-MH cell of pouch type with PVA/AG/50%KOH electrolyte.

As described in the Experimental, the cells were in the form of elastic pouch type sets. This flexible construction is much different from that with rigid prismatic or cylindrical cells. In the flexible pouch type cell the electrodes are alternately layered and separated by the alkaline polymer electrolyte making a stack of electrodes closed by the vacuum sealer, at the same time removing possible liquid phase from the cell. In a typical Ni-MH electrodes and the separator are immersed in the water solution of the electrolyte and contained in a tightly closed case. The use of a typical liquid electrolyte 6M KOH in Ni-MH pouch cells is technologically inconvenient and does not permit correct run of the electrochemical processes in the cell. The impossibility of using excess of liquid electrolyte in pouch type construction does not permit correct cell work and all attempts at introducing excess of liquid phase into a pouch type cell prevent their flexible construction.

Fig.8 and Fig.9 present exemplary charge/discharge curves in the third cycle of work of the model Ni-MH cells.

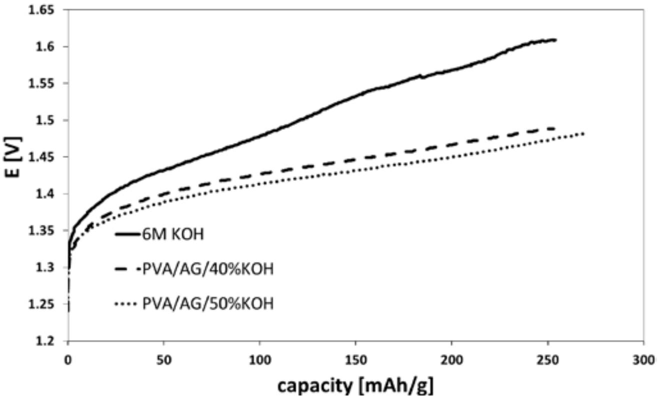

Fig. 8. Exemplary charge curves recorded for model Ni-MH pouch cells in the 3rd cycle of work.

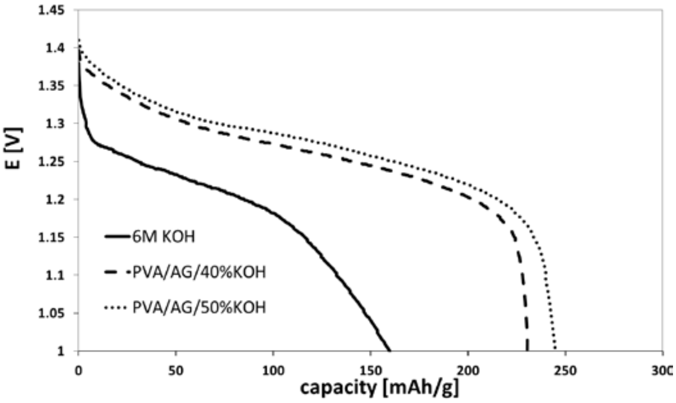

Fig.9. Exemplary discharge curves recorded for model Ni-MH pouch cells in the 3rd cycle of work.

The discharge capacities of the systems with pouch cells containing alkaline polymer electrolytes reach higher values of about 250mAh/g, when compared to the cells with classical separator and liquid (6M KOH) electrolyte. Moreover, the former show much higher stability of work in the cycles of charge and discharge of the system (Fig.10).

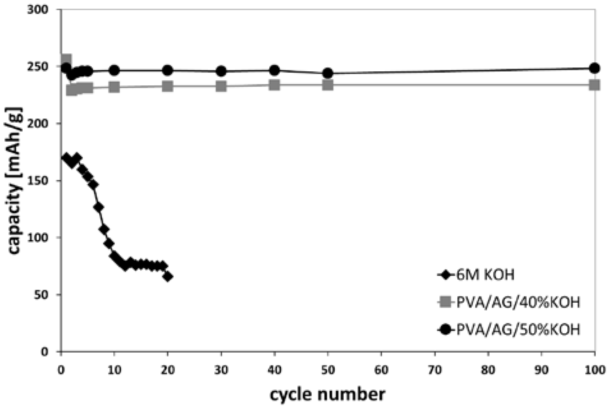

Fig.10. Comparison of discharge capacity obtained from 1g of the active mass of negative electrode for model Ni-MH pouch type cells as a function of the number of charge/ discharge cycles.

4 Conclusion

The polymer membrane composed of vinyl polyalcohol and agar as a gelating medium, at the PVA : AG wt. ratio of 1:3, was proved to be a stable polymer matrix for alkaline electrolyte. The alkaline polymer electrolytes composed of PVA/AG/KOH with KOH content in the range 0-50%wt., obtained by physical cross-linking, occur in the form of ion-conducting polymer membranes, characterized by similar thermal stabilities and similar surface structures. The addition of agar to PVA-KOH allows the polymer complex to absorb more KOH preserving the stability of the membrane solid phase, which leads to increased ionic conductivity. The addition of agar may also improve water retaining and mechanical properties of the polymer electrolyte based on PVA. At 25°C the conductivity of the alkaline polymer electrolyte with the highest content of KOH reaches a value close to 0.25 Scm^{-1} (PVA/AG/50%KOH).

After dehydration and then immersion in distilled water for 3 h, the polymer electrolyte samples PVA/AG/KOH undergo full regeneration of their physicochemical and electrochemical properties, which is very important especially when the batteries are meant to be stored for a long time, e.g. in special applications.

The model cells with alkaline polymer electrolytes PVA/AG containing 40% wt. and 50% wt. KOH show high stability of work, in particular much higher than that of Ni-MH cells in pouch type constructions filled with liquid electrolyte.

As evidenced by the electric studies of the model Ni-MH pouch type cells, it is possible to use in them alkaline polymer electrolyte composed of PVA, AG, KOH. Moreover, addition of gelating agent -agar- permits incorporation of a greater amount of water KOH solution, so improved transport of ions and enhanced stability of the electrochemical system. The use of alkaline polymer electrolytes with agar also improves the safety of work and operation of the Ni-MH cells, among others, it permits other than classical vertical type of electrodes arrangement needed when working with liquid electrolyte.

In conclusion, according to the results of our study, the alkaline polymer electrolytes obtained with the use of agar show suitable physicochemical and electrochemical properties for considering their application in flexible, prismatic Ni-MH batteries.

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