Polish J. Chem., **75**, 1719–1728 (2001)

Electrochemical Properties of Cells with Conducting Polymers and Nafion® Membrane

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(Received May 16th, 2001)

Electrochemical properties of cells, comprising electronically- and ionically-conducting polymers, were studied using open sandwich electrode systems of cation exchanging polypyrrole or poly(N-methylpyrrole) doped by poly(4-styrenesulphonate) ions or Nafion (PPy(PSS) and PMPy(PSS) or PPy(Nafion) and PMPy(Nafion) respectively). The electrolyte/separator used was Nafion 117 membrane. These cells were characterized by a stable open circuit voltage (in the absence of oxygen), possibility of repeated charge/discharge and capacity of order 10 C/g of polymeric materials. Therefore, these systems are promising for practical applications in all plastic battery construction using conducting polymers.

Key words: conducting polymers, polypyrrole, poly(N-methylpyrrole), Nafion, batteries

Recently a growing interest in small, safe, reliable and non-toxic electrochemical power sources of high energy density is observed. Modern lithium-ion batteries, proved to be currently one of the best available options, are used in numerous popular electronic devices. Actually, it is still a great challenge to design all solid state batteries free from a liquid electrolyte. Instead of the liquid phase, thin ionically conductive membranes can be used. Thus, the possibility of leakage and corrosion is minimised, as well as the battery miniaturization is easier [1,2,3]. The example of this set up, already available commercially, are lithium-polymer batteries, containing lithium anode and ionically conducting membrane.

From the point of view of charge and energy storage, interesting properties are offered by electronically conducting polymers, as polyacetylene, polypyrrole or polyaniline [4]. These materials were used in the battery construction, *e.g.* [5,6,7]. In line with polymer batteries, all solid and all plastic batteries were proposed: the electrodes are conducting polymers, while ionically conducting gel [8,9] or Nafion [10] serves as membrane-separator.

The aim of this work is to study properties of cells, composed of electronically- and ionically-conducting polymers, which potentially can be used in all plastic battery construction. The tested cells contained polypyrrole and poly(N-methylpyrrole) as electrode materials and Nafion 117 membrane as an electrolyte/separator. The cation exchanging polymer films, doped by poly(4-styrenesulphonate) ions, were ap-

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plied – thus the ion exchange between the polymer electrode materials and cation conducting Nafion phase is enabled. This set up was expected to facilitate the process of charging/discharging of the cell. For comparison, a similar system composed of polypyrrole and/or poly(N-methylpyrrole) layers doped with Nafion were also tested. In this case Nafion plays a double role: of a polyelectrolyte doping anion (from negatively charged sulphonate groups) giving rise to the cation exchanging properties of the polymers, as well as of ionically conductive membrane. The absence of a distinct interface: conducting polymer phase/Nafion membrane in this case (the polymers were deposited inside the Nafion layer), should facilitate the cation transport between the conducting polymer electrodes.

EXPERIMENTAL

The electrochemical measurements, involving cyclic voltammetry and chronopotentiometry, were performed both in the presence and in the absence of electrolyte solution, using EG & G PARC potentiostat/galvanostat 273 A. In the former case a conventional electrochemical cell with a working glassy carbon disk electrode of diameter 3 mm, as the substrate for polymeric coatings, a silver/silver chloride in 1 M KCl gel reference electrode and a platinum counter electrode were used. For other experiments, performed both in the absence and the presence of electrolyte solution the measurements were carried out in a two-electrode open sandwich system (Fig. 1), composed of two semi-circle glassy carbon electrodes of the total surface area 0.07 cm^2, separated by a 1 mm insulator gap.

Distilled pyrrole and N-methylpyrrole (Aldrich) were kept refrigerated and prior the use they were purified by passing through an alumina gel mini-column. Nafion 117 solution (5% solution in lower aliphatic alcohols, Fluka) was used as received. Millipore water was used throughout this work. The other chemicals (Aldrich or Fluka, p.a.) were used as received. All measurements were made at ambient temperature (21°–24°C). Polypyrrole and poly(N-methylpyrrole) were deposited potentiostatically at $E = 0.8$ V or galvanostatically (current density: 0.1 mA cm^{-2}) on electrodes, previously polished by Al_2O_3, 0.3 μm. The thickness of the polymer film can be evaluated, assuming that the polymerization charge 24 mC

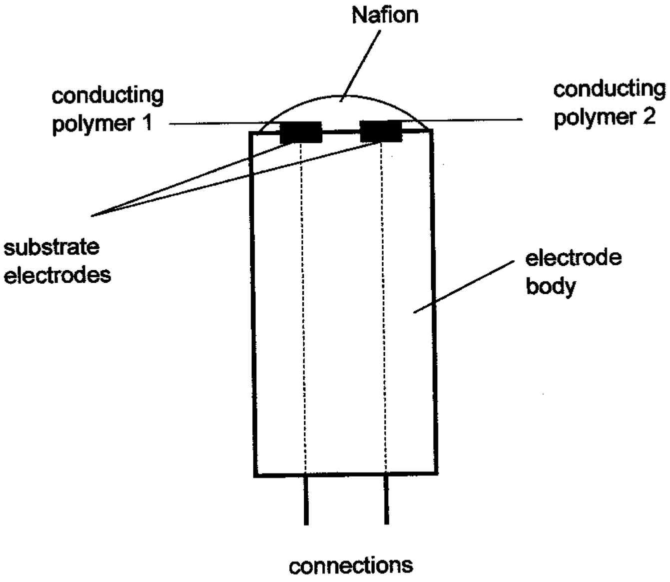

Figure 1. Scheme of the open sandwich electrode system.

cm^{-2} corresponds to deposition of 0.1 μm film [11]. The electrodes used in the experiments were modified with conducting polymer layers or with conducting polymers and Nafion® according to one of the two procedures:

Procedure 1. The polypyrrole and poly(N-methylpyrrole) layers doped by PSS$^-$ ions (PPy(PSS) and PMPy(PSS) resepectively) were deposited potentiostatically from 0.05 M pyrrole (or N-methylpyrrole) + 0.1 M sodium poly(4-styrenesulphonate) solution, directly onto the glassy carbon disc electrode. Then the electrode was rinsed with water, dried in the air, then covered by 5 μL of Nafion 117 solution. The coated layer (of thickness close to 2 μm [12]) was allowed to dry under ambient conditions. As a result, the bilayers: PPy(PSS)/Nafion and PMPy(PSS)/Nafion were obtained.

Procedure 2. The Nafion layer was coated onto a bare substrate electrode (by covering with 5 μL of Nafion 117 solution) and left to dry under ambient conditions. The electrode with dry Nafion layer was placed in the 0.05 M monomer solution containing 0.1 M $NaClO_4$ supporting electrolyte. The conducting polymer film (polypyrrole or poly(N-methylpyrrole)) was deposited galvanostatically inside the pre-coated Nafion layer, to obtain PPy(Nafion) and PMPy(Nafion) respectively. Since the Nafion layer was thicker than that of conducting polymer, the system obtained was a kind of bilayer: conducting polymer doped with Nafion/Nafion with a transition interface.

The above procedures were also used in a two electrode open sandwich set up (Fig. 1). Either the polymers doped by PSS$^-$ ions were deposited on each semicircle electrode and the whole area (including the gap) was covered with Nafion solution (procedure 1) or the polymers were electropolymerized, independently on both semicircle electrodes, inside the previously coated Nafion membrane, covering both electrodes (procedure 2). Prior to measurements the sandwich systems were conditioned by cycling each electrode in electrolyte solution (1 M KCl unless otherwise stated), within the potential range –0.8 ÷ 0.5 V, with the scan rate 50 mV s^{-1}. The solutions under study were deoxygenated using argon. The two-electrode system, without solution, was deoxygenated by sealing the cell using Parafilm, under argon flow.

RESULTS AND DISCUSSION

Conducting polymers/Nafion bilayers: Polypyrrole and poly(N-methylpyrrole) layers doped by PSS$^-$ ions (PPy(PSS) and PMPy(PSS) respectively) were obtained on a bare electrode and then modified by Nafion according to the procedure 1. The voltammetric curves recorded for PPy(PSS)/Nafion or PMPy(PSS)/Nafion bilayers are shown in Fig. 2. The currents recorded for these systems practically did not differ from those obtained for the polymers non-modified by Nafion. This result shows that the presence of the external Nafion layer is not inhibiting the ion transfer processes between the conducting polymer and the solution. Most probably this effect results from cation exchanging properties of both conducting polymer films (PPy(PSS) and PMPy(PSS)) and Nafion layer. Therefore, oxidation/reduction of these polymers is connected with release/incorporation of cations, which can be easily transferred across the cation conductive Nafion layer. The difference observed in electroactivity range between PPy(PSS)/Nafion and PMPy(PSS)/Nafion is higher than 0.5 V (curves 1 and 2, Fig. 2), the same as in the absence of Nafion layer. After integration of the voltammetric curves of polymers modified by Nafion layer, the oxidation/reduction charges of the polymer systems can be obtained. The redox process charge linearly increases with the rising polymerization charge of the layer, *i.e.* it is proportional to the layer thickness (Fig. 3). The polymerization charge 10 mC corresponds to the thickness about 0.6 μm [11]. The slope of the dependence presented in Fig. 3 for PMPy(PSS)/Nafion is lower than for PPy(PSS)/Nafion because the former polymer is oxidized to a lower extent than polypyrrole under voltammetric conditions.

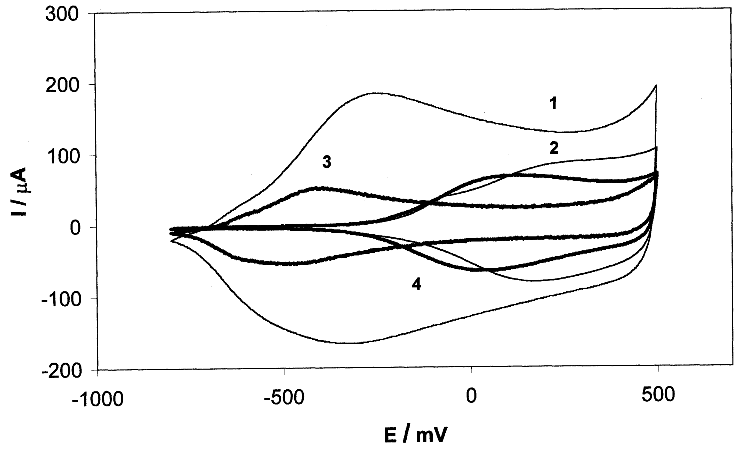

Figure 2. Cyclic voltammetric curves of PPy(PSS)/Nafion (1), PMPy(PSS)/Nafion (2), PPy(Nafion) (3) and PMPy(Nafion) (4) in 1 M KCl. Scan rate: 50 mV s^{-1}. Polymerization charges: (1): 25 mC, (2): 25 mC, (3): 4 mC, (4) 12 mC.

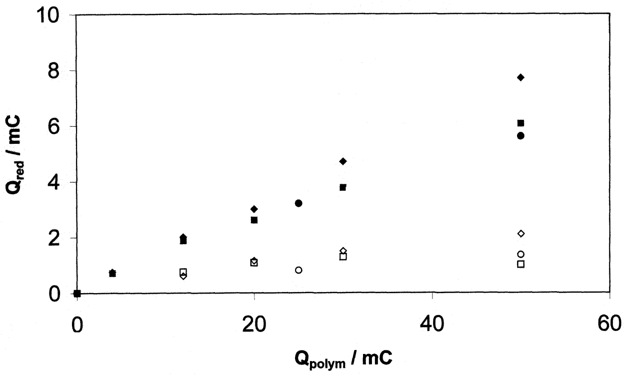

Figure 3. The dependence of the reduction charge obtained from cyclic voltammetry (reduction charge equal to the oxidation charge) with scan rate 50 mV s^{-1} (CV) or chronopotentiometry with applied current 0.05 mA (CP) on polymerization charge of polymers: PPy(PSS)/Nafion (CV) (filled circles), PPy(Nafion) (CV) (filled squares), PPy(Nafion) (CP) (filled rhombs), PMPy(PSS)/Nafion (CV) (open circles), PMPy(Nafion) (CV) (open squares), PMPy(Nafion) (CP) (open rhombs).

The redox capacity of PPy(PSS)/Nafion and PMPy(PSS)/Nafion was additionally analyzed using chronopotentiometry. Initially, the film was polarized at 0.5 V (corresponding to the oxidized state of the polymers) for 30 s and then a cathodic current was applied. From these experiments the reduction charge was obtained (as a product of transition time and the applied current). Within the limits of experimental error the charges obtained were equal to the reduction ones calculated by integration of the voltammetric curves. For PMPy(PSS)/Nafion system, with the PMPy(PSS) polymerization charge higher than 80 mC, both values obtained from voltammetry and chronopotentiometry decrease with rising thickness of the film, pointing to limitation of ion transport in thick PMPy layers.

The characteristic properties of PPy(PSS)/Nafion and PMPy(PSS)/Nafion bilayers: the difference in electroactivity range (Fig. 2); the increase of the accumulated charge with rising polymer layer thickness (Fig. 3); the high ionic conductivity of Nafion layer; as well as lack of hindrances in ion transport resulting from the presence of Nafion membrane – are promising for application of these polymers in battery systems construction.

Experiments analogous to the described above were also done for electrodes, modified by polymers doped with Nafion, according to the procedure 2, *i.e.* for polymers obtained inside the Nafion membrane. In the course of galvanostatic polymerization, an initial potential decrease is observed, however, for polymerization times longer than 1 min., the changes of the potential are rather small. The polymerization potential of poly(N-methylpyrrole) on the Nafion coated electrode is about 0.25 V higher than the corresponding potential for polypyrrole, similarly as for electrodeposition in the presence of dopant in the solution. It should be noted that the polymerization conducted on electrodes modified with Nafion occurs at significantly lower potentials than in the absence of Nafion layer, the difference between the polymerization potential for non-modified and modified electrode is higher than 0.2 V. This effect can be explained by the properties of Nafion, this membrane contains negatively charged $-SO_3^-$ groups, which act as doping ions, facilitating the polymerization process and providing an improvement of charge transfer in the polymer [13,14,15,16]. The voltammetric curves of the polymers doped with Nafion are presented in Fig. 2. The peaks for polymers obtained inside the Nafion membrane, for PPy(Nafion) and PMPy(Nafion) are well shaped and their electroactivity potential range is moved about 0.3 V towards lower potentials in comparison to the polymers obtained on the bare electrodes. Thus, polymerization conditions (dopant) highly affect the properties of the polymers obtained. Due to presence of immobilized sulphonate groups, the cation exchanging properties are exposed, similarly as for PPy(PSS) and PMPy(PSS).

The oxidation/reduction charges, obtained after integration of voltammetric curves recorded for PPy(Nafion) and PMPy(Nafion), are linearly dependent on the polymerization charge of the polymers, *i.e.* on their thickness (Fig. 3), with the slopes similar to those for PPy(PSS)/Nafion and PMPy(PSS)/Nafion systems, respectively. Analogously to PPy(PSS)/Nafion and PMPy(PSS)/Nafion bilayers, the slope recorded for PMPy(Nafion) is lower than the one observed for PPy(Nafion), because in the latter case the polymer is oxidized to a lower extent under voltammetric conditions, a lower doping level of the polymer is achieved. Moreover, for PMPy(Nafion) of polymerization charge higher than 20 mC the redox charge decreases, due to some hindrances in ion transport inside the thicker layer. Similarly to PPy(PSS)/Nafion and PMPy(PSS)/Nafion the charge accumulation in PPy(Nafion) and PMPy(Nafion) was also analyzed using chronopotentiometry, under conditions described above. Fig. 3 presents comparison of redox charges calculated from voltammetric curves and reduction charges obtained from chronopotentiometry experiment. The reduction charge obtained from chronopotentiometry is slightly higher than the redox charge from cyclic voltammetry, pointing to a more advanced reduction in the former case, due to a longer time of forced reduction. The difference is more significant for thick PMPy(Nafion) polymer films, because for polymerization charges higher than 20 mC the reduction charge continuously rises, in contrary to the results obtained from cyclic voltammetry.

The difference in electroactivity range of PPy(Nafion) and PMPy(Nafion) is higher than 0.5 V (curves 3 and 4, Fig. 2) and is similar to that observed for PPy(PSS)/Nafion and PMPy(PSS)/Nafion. Moreover, the linear dependence of the redox (or reduction) charge on the polymer film thickness shows that these polymers can be also potentially applicable as electrode materials to construct all polymeric batteries.

Sandwich systems of modified electrodes: The first open sandwich system (cell) studied was obtained by coupling the bilayer systems obtained according to the procedure 1 (polymerization in the presence of PSS^- ions and coating of Nafion membrane). One semi-circle substrate was coated by PPy(PSS), the other one by PMPy(PSS) and the whole area was coated by Nafion to obtain the cell: PPy(PSS) | Nafion | PMPy(PSS). Fig. 4 presents comparison of voltammetric curves recorded for the sandwich system immersed in the electrolyte solution (1 M KCl) and then, for the same system, withdrawn from the electrolyte solution. In the absence of solution the currents are lower than in the former case, regardless the experiment conditions the peaks at potentials higher than 0.4 V (PMPy(PSS) *vs*. PPy(PSS)) were observed, pointing to the electroactivity of the system in the absence of external electrolyte solution. It can be presumed that the electroactivity of the system will be preserved unless the Nafion layer is not completely dry. In the dry membrane the ion transfer is blocked and the system loses its electroactivity, thus the initial cycling is of high importance. After conditioning of the cell by cycling in 1 M KCl solution, the cell was polarized by the voltage 0.5 V (PMPy(PSS) *vs*. PPy(PSS)) until no detectable current was recorded. Then the circuit was disconnected and the open circuit voltage was measured in time, under deaerated conditions. The decrease of the measured voltage,

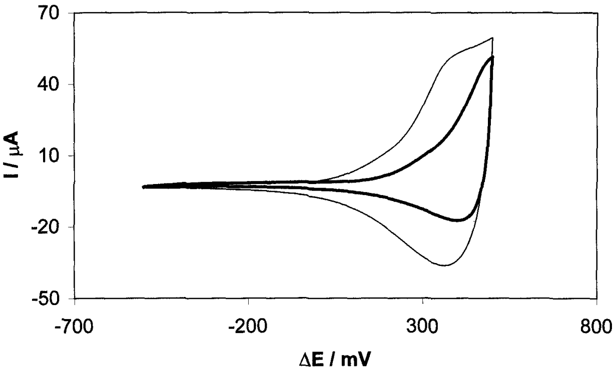

Figure 4. Cyclic voltammetric curves of two electrode sandwich system: PPy(PSS) (polymerization charge: 50 mC) | Nafion | PMPy(PSS) (50 mC) in 1 M KCl solution (thin line) and then in the absence of the solution (thick line). Scan rate: 50 mV s^{-1}.

starting from the 0.5 V value was small, reaching 480 mV after 10 minutes, then the voltage was practically constant, pointing to stability of the stored charge. In the presence of oxygen the observed voltage decrease was much faster, due to spontaneous oxidation of polypyrrole.

The forced discharge of the cell was tested, using different values of the applied current. The discharge time decreases with increasing current used (Fig. 5). Although the current value applied was changed about 5 orders of magnitude, the dependence of the measured voltage *vs*. time was close to linear, pointing to a capacitive behaviour of the sysytem. For the currents not higher than 10–6 A, after 5 minutes of forced discharge the voltage decreased to about 0.25 V. If the higher current value was applied to the system, a rapid complete discharge was observed after more than 100 s. Repeated (4 times) steps: charging/discharge practically did not change the shape of the voltage *vs*. time dependences. The multiplication product: applied current · time needed to obtain the voltage 0 V gives the charge, which can be obtained from the cell. The resulting value 0.42 mC was compared with the charge calculated from chronopotentiometric experiments for PPy(PSS)/Nafion and PMPy(PSS)/Nafion (of the same thickness as the polymers in the cell), the charge was 12 mC and 1.4 mC respectively. Thus the charge released from above described cell is about 1/30 of the reduction charge of PPy(PSS)/Nafion and 1/3 of the charge stored in the bilayer PMPy(PSS)/Nafion. This result shows that the charge release efficiency in the open sandwich system is determined by the redox capacity of the PMPy(PSS) layer. The obtained efficiency is lower than 1, resulting from the voltage applied (0.5 V) to charge the cell, for a higher voltage it can be higher. Additionally, as the current flows, limitations in ion transport in the Nafion membrane and on polymeric interfaces in the absence of the solution are observed, the currents values in the absence of the electrolyte are about 1/3 of the one recorded in the electrolyte solution (*cf*. Fig. 4). Therefore, it could be expected that the kind of electrolyte, used in the system pre-treatment (conditioning), would affect the efficiency of the system. The results obtained for the

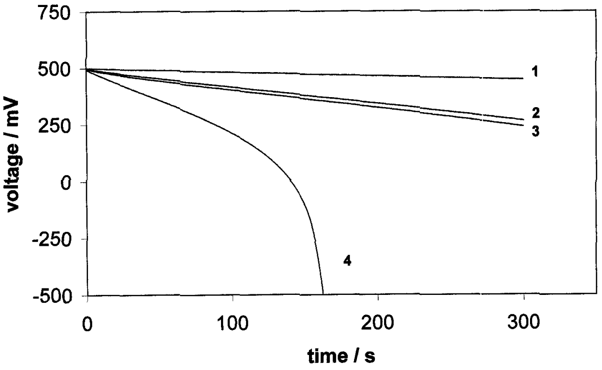

Figure 5. Discharge curves of the PPy(PSS) (polymerization charge: 100 mC) | Nafion | PMPy(PSS) (50 mC) sandwich system, applying a current: 2 × 10^{-11} A (1), 10^{-8} A (2), 10^{-6} A (3) and 3 × 10^{-6} A (4).

cells conditioned by cycling in 1 M KCl and 0.1 M KCl solutions, as well as in 0.1 M LiCl and 0.1 M HCl show that the highest charges stored in the cell are obtained after conditioning in 1 M KCl solutions. In this case the high concentration of mobile K^+ ions, providing a loading of the membrane with electrolyte cations, results in a high ionic conductivity of Nafion and a facile ionic transport, as well as incorporation/release of cations by PPy(PSS) and PMPy(PSS) layers.

For comparison a system composed of two PPy electrodes: PPy(PSS) | Nafion | PPy(PSS) was also tested. After 15 minutes the recorded voltage decreased from 0.5 V to 0.45 V. Due to the self-discharge process related to polymers applied, the open circuit voltage was less stable than for the former system composed of PPy(PSS)/Nafion and PMPy(PSS)/Nafion. This effect results from identical formal potentials of both electrode materials. Under forced discharge conditions the PPy based cell voltage decreased linearly with time (Fig. 6) as for the previous cell, PPy(PSS) | Nafion | PMPy(PSS). However, the charges obtained in this case were higher, even for the highest applied current (3×10^{-6} A) the cell voltage decreased only to 0.25 V after 5 minutes. This effect can be attributed to the absence of the PMPy(PSS) layer, efficiency limiting element of the whole system. Therefore, due to the high ability of PPy(PSS) to store the electric charge, enhanced by the possibility of depositing thick electroactive layers, the PPy based system is especially interesting in application context, even though the self-discharge properties.

The above systems were compared to the open sandwich one, where both conducting polymers were doped with Nafion (according to the procedure 2). One electrode was covered by PPy (polymerization charge: 8 mC), the other one, by PMPy (polymerization charge: 22 mC); the cell obtained: PPy(Nafion) | Nafion | PMPy(Nafion). As a consequence, no distinct interface between the Nafion membrane and the conducting polymer phase was created. Thus, this system was expected to be superious over the PPy(PSS) | Nafion | PMPy(PSS).

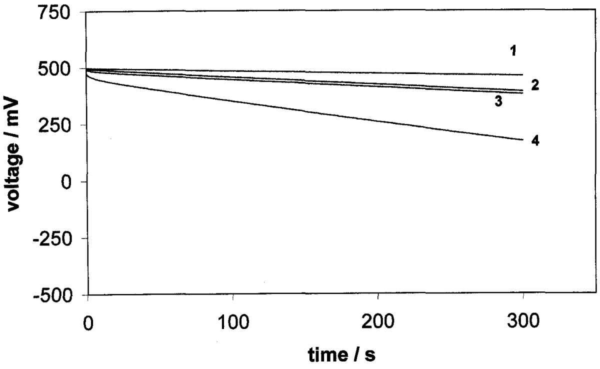

Figure 6. Discharge curves of the PPy(PSS) (polymerization charge: 100 mC) | Nafion | PPy(PSS) (100 mC) sandwich system, applying a current: 2×10^{-11} A (1), 10^{-8} A (2), 10^{-6} A (3) and 3×10^{-6} A (4).

The voltammetric curves recorded in this two-electrode system, both in the presence and in the absence of electrolyte solution were similar as for the cell composed of PPy(PSS) and PMPy(PSS) separated by Nafion. The currents recorded in the absence of solutions were 3–4 times lower, however the peaks were still observed in the same potential range. Similarly to the former system, with PSS^- doped conducting polymers, this cell was electroactive only if the Nafion layer was not completely dry. This observation is in line with the conclusion about the transport possibility in the separator phase. After pretreatment the system by cycling in 1 M KCl solution a voltage 0.5 V was applied until no detectable current was recorded. Then, the resulting open circuit voltage was followed in time, the decrease of the voltage below 0.5 V was faster than for PPy(PSS) | Nafion | PMPy(PSS), close to 10 mV min^{-1}, reaching a stable value about 0.4 V.

The forced discharge of the cell was also tested. Similarly, as for the cells comprising polymers doped with PSS^- ions, the discharge time decreases with rising current (Fig. 7). The obtained responses were similar to the ones obtained for PPy(PSS) | Nafion | PMPy(PSS) systems. The linear dependences voltage vs. time were recorded, although in the Nafion doped polymers case the slopes of lines were higher, resulting from lower thickness of the conducting polymer layers. For discharge currents 10^{-8} and 10^{-6} A , after 300 s of discharge the output voltage was close to 0.25 V, while for the current equal to 3×10^{-6} A the complete discharge was observed after about 80 s. The charge related to the cell discharge for the latter current used is close to 0.25 mC, i.e. is equal only to about 1/5 of the charge stored in single PMPy(Nafion) layer, obtained from chronopotentiometric experiments (1.4 mC and 1.2 mC for PPy and PMPy respectively, Fig. 3). This result is similar to that obtained for the cell with PPy(PSS) and PMPy(PSS), supporting the thesis of charge transfer limitations in the PMPy layer, regardless the dopant used.

The properties of the above cell: PPy(Nafion) | Nafion | PMPy(Nafion) were compared with the systems composed of two PPy electrodes (of polymerization charge: 4

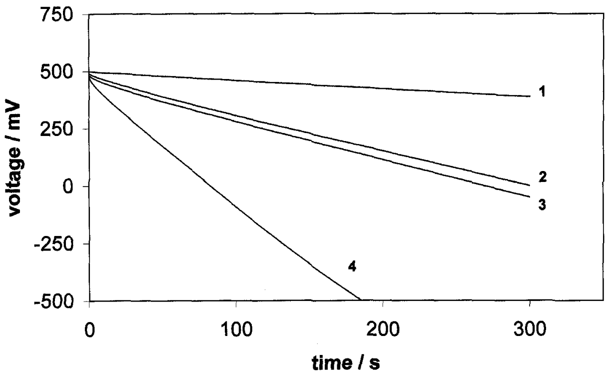

Figure 7. Discharge curves of the PPy(Nafion) (polymerization charge: 8 mC) | Nafion | PMPy(Nafion) (22 mC) sandwich system, applying a current: 2×10^{-11} A (1), 10^{-8} A (2), 10^{-6} A (3) and 3×10^{-6} A (4).

mC), the polymers were doped with Nafion: PPy(Nafion) | Nafion | PPy(Nafion). The open circuit voltage, measured after polarization at 0.5 V in the latter case, is less stable than in the PPy(Nafion) | Nafion | PMPy(Nafion) system. It decreases to about 0.2 V after 15 minutes. This effect results from identical formal potentials of both electrodes material, reaching a common average oxidation state. This process is most probably facilitated by the same dopant-separator. In the case of forced discharge,

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