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Cobaltabisdicarbollide anion $[Co(C_2B_9H_{11})_2]^-$ as doping agent on intelligent membranes for ion capture

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Abstract

It has been proven that the non-nucleophilic, low charge density and weakly coordinating cobaltabisdicarbollide anion $[Co(C_2B_9H_{11})_2]^-$, can be highly relevant as dopant for conducting organic polymers. We have developed a new material based on polypyrrole (PPy) which uses the cobaltabisdicarbollide anion as a doping agent. This anion provides enhanced properties to PPy, the most striking one is the high over oxidation resistance. The high volume of $[Co(C_2B_9H_{11})_2]^-$ imposes low mobility inside the polymeric matrix thus preventing dopant leakage when a reducing potential is applied on the material. Under these conditions the cation capture (Eq. 1) prevails during the reversible electrochemical redox process, also called doping–undoping. $[PPy^{n+}(A^-)_n]+nC^+ + ne^- \Delta [PPy(A^-)_n(C^+)_n]$. The membrane is highly sensitive to the cationic volume of the solute. This property has allowed to develop cationic selective membranes by control of the applied reducing potential. The chronocoulometries registered during the charge–discharge process show an almost perfect reversibility of cation exchange process and no detectable degradation of the membrane due to dopant loss or over oxidation even after 40 successive cycles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Selectivity; Weakly coordinating anions; Conducting organic polymers; Polypyrrole

1. Introduction

Since their discovery, two decades ago there has been great interest in the development of organic conducting polymers (COP's). Due to the great number of new potential applications [1–3], such as micromechanical [4] or electrooptical display devices [5], electrochemical selective electrodes [6–10], radiation shields [11], or as a cathode for rechargeable batteries [12] just to mention a few. Recently, some examples of polypyrrole (PPy) films applied as intelligent membrane systems for cation binding and release have also been reported [13,14]. The challenge of these membranes is the possibility to act as traditional ion exchange resins but controlling the ionic capture and posterior regeneration by electrical stimulation. The operation of these membranes is based on the existence of two reversible redox states in PPy and their easy interconversion. Two extreme circumstances could take place (equations 1 and 2):

i) Cation exchanger membrane (Eq. 1).
ii) Anion exchanger membrane (Eq. 2).

$$[PPy^{n+}(A^-)_n] + nC^+ + ne^- \rightleftarrows [PPy(A^-)_n(C^+)_n] \qquad (1)$$

where, A^- is large volume, low mobility dopant; C^+ is cation from electrolyte.

$$[PPy^{n+}(A^-)_n] + ne^- \rightleftarrows PPy + nA^- \qquad (2)$$

where, A^- is small volume, high mobility dopant.

Large volume dopants exhibit low mobility inside the polymer matrix. In these conditions the electrochemical reduction forces cation capture to keep electroneutrality (equation 1). The relative amount of cation–anion exchange, in and out of the membrane, greatly depends on the nature of the dopant [15–19]. Therefore, new materials could be tailored on purpose to remove certain components from a multi-component mixture [20].

The aim of this work is the preparation of cation capture membranes based on cobaltabisdicarbollide

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$[Co(C_2B_9H_{11})_2]^-$ doped PPy with the enhanced properties previously reported by our group [21]. The high over oxidation resistance provided by the cobaltabisdicarbollide [21] represents a significant improvement in the long term stability of such membranes usually doped with large volume organic sulfonates [22,23]. The irreversible attack of OH^- to the polymer chain, which is responsible for the PPy degradation, when high potentials are applied to the membrane, will be significantly reduced with the use of the cobaltabisdicarbollide anion. It will allow to significantly increase the regeneration potential of the membrane in the anodic direction, where conventional PPy's suffer degradation processes. This over potential will increase the regeneration efficiency and substantially decrease the necessary time to perform it.

In the work reported in this paper, we did benefit from these advantageous characteristics to study the possible selectivity in cation capture of these materials.

2. Experimental

2.1. Materials

All chemicals used for this study were purchased from Aldrich Chemicals, except de cesium salt of cobaltabisdicarbollide $Cs[Co(C_2B_9H_{11})_2]$ obtained from Katchem. Pyrrole (Py) was distilled under reduced pressure prior to use and stored in nitrogen atmosphere in the dark at 0 °C. Aqueous solutions were 0.1 M in the electrolyte (except where noted). All solutions were deoxygenated by purging them with nitrogen for 10 min.

2.2. Instrumentation and preparation of $PPy[Co(C_2B_9H_{11})_2]$

EG&G Princeton Applied Research PAR273A potentiostat–galvanostat were used in all electrochemical experiments. $PPy[Co(C_2B_9H_{11})_2]$ films for cyclic voltammetry experiments were galvanostatically grown over a 3 mm Ø glassy carbon electrode in a double compartment cell with a standard three electrode system at 0.3 mA. PPy films for cation capture measurements were polymerized over 1 cm^2 stainless steel electrode (Fe Cr 18 Ni 10 steel 1431) at 2.5 mA. The extent of film growth was determined by the number of Coulombs passed during polymerization (90 mC for cyclic voltammetry and chronocoulometries experiments and 16.6 C for cation capture measurements). Platinum wire was used as a counter electrode in all experiments. Ag/AgCl (10% $KCl \cdot H_2O$) and Ag/AgCl (0.1 M $(But)_4NCl \cdot CH_3CN$) were used as reference electrodes in aqueous media and in acetonitrile solutions, respectively. Solutions for electropolymerization were 0.1 M in Py and 0.035 M $Cs[Co(C_2B_9H_{11})_2]$ in acetonitrile 1 wt.% water. After polymerization, PPy membranes were rinsed in fresh acetonitrile and then transferred to the aqueous media for 10 min before electrochemical measurements.

2.3. Cyclic voltammetry studies

PPy electrochemical characterizations by cyclic voltammetry were performed in a single compartment cell, 0.1 M supporting electrolyte at a scan rate of 20 mV s^{-1}, in a potential range from −1.6 to 0.5 V versus Ag/AgCl (10% $KCl \cdot H_2O$).

2.4. Selectivity studies

PPy selective cation capture quantification was performed by membrane potentiostatic reduction at single voltages in the range from −0.4 to −1.4 V versus Ag/AgCl (10% KCl H_2O) in LiCl 0.1 M, KCl 0.1 M and LiCl 0.1 M+KCl 0.1 M aqueous solutions. After the electrochemical reduction, PPy membranes were rinsed in deionized water and vacuum dried for at least 3 h.

In another set of experiments, three membranes were immersed in the three electrolytes described above for 1 h. For comparative purposes, no reducing potential was applied in the aim to know the interactions between the ions in solution and the film.

The dry PPy films were carefully removed from the electrode surface, weighted and mineralized by nitric acid digestion. Each PPy membranes was put in individual Kjeldhal tubes, then 25 ml of 30% nitric acid solution was added to every tube and the mixtures heated until quasi-total dryness. When cold, 20 ml of 15% nitric acid were added and heated again. This last process was repeated four times, until no organic material was present and the orange color (typical of cobaltabisdicarbollides derivatives) disappears. The light red (evidencing Co presence) resulting solution was diluted to 100 ml.

Quantification of Li, K and Co was performed by flame atomic absorbance spectrophotometry at 670.8, 766.5 and 242.5 nm, respectively. Li quantification was directly measured from the original solution, Co and K measurements were done diluting 1/10 the original solution. Perkin–Elmer 1100 flame atomic absorption spectrophotometer was used in all measurements.

2.5. Stability measurements

Ion capture stability towards degradation or dopant irreversible loss was tested by 40 successive oxidation–reduction cycles applying a constant potential (0 and −0.65 V, respectively), in a NaCl 0.1 M solution.

3. Results and discussion

3.1. Cyclic voltammetry characterization

A typical cyclic voltammogram (CV) obtained with PPy[Co($C_2B_9H_{11}$)$_2$] in NaCl 0.1 M aqueous electrolyte is shown in Fig. 1b. Three different regions can be defined in the CV plot. Regions I and II show well defined waves, since the first cycle, with high peak intensities. On the contrary, region III shows an ill-defined wave with lower current intensity. This last wave does not appear in the first CV cycle, but slowly increases in each new cycle achieving its maximum intensity after 30 cycles.

Fig. 1a shows the cobaltabisdicarbollide cyclic voltammetry (Co^{2+}/Co^{3+} transition) performed in aqueous solution of NaCl 0.1 M overlapped to this obtained for PPy[Co($C_2B_9H_{11}$)$_2$] (Fig. 1b). The cobaltabisdicarbollide wave almost perfectly matches the region I wave in the polymer, and therefore, confirming the $[Co(C_2B_9H_{11})_2]^-$ doping.

In an earlier paper [21] we assigned the region II wave to the cation insertion–deinsertion on the basis of the electrochemical performance of PPy[Co($C_2B_9H_{11}$)$_2$] in bulky cation electrolytes such as tetrabutylammonium chloride (TBACl) that shows electrochemical processes inhibition. This result was interpreted as the impossibility of charge compensation when reducing the material due to the low diffusion rate inside the membrane of these bulky cations. In order to confirm this result some additional experiments have been performed.

The electrochemical processes inside the polymer are kinetically limited by the ionic diffusion rate in the polymer matrix, much slower than the ionic diffusion rate in solution. To know the direction course of ionic exchange, during reduction in region II (from polymer to solution or from solution to polymer), the solution diffusion rate was decreased by increasing the liquid viscosity by gelatin addition. Fig. 2 shows the cyclic voltammetry plots in sodium naftalenesulfonate electrolyte with increasing ratios of gelatine (0, 1, 3 and 5%, respectively). The dopant wave does not appear because the CV's are performed in a more anodic region that the previous experiments. The increasing viscosity clearly affects the position and intensity of the reduction wave (from −1.13 to −1.30 V) but has less noticeable effect in the oxidation peak position. As the viscosity increases, ionic exchange becomes more difficult and higher negative potentials are necessary to reduce the material. Therefore, as the only difference between these experiments is the diffusion rate in solution, it comes out that the ionic exchange during the reduction process occurs in the direction of the solution to polymer. Therefore, the charge compensation during reduction in region II has to be done by cationic uptake from the electrolyte. The small oxidation potential drift should not be attributed to a more difficult cation release from polymer to solution because the peak displacement is in the cathodic direction. This shift to less anodic potentials could be simply attributed to an incomplete reduction process.

Additional evidences for cation exchange in region II were provided by cyclic voltammetry in alkaline chloride solutions. Fig. 3 shows CV's in LiCl, NaCl, KCl, RbCl and CsCl 0.1 M solutions. The aqueous cation volume has, once again, great influence in the potential reduction peak position (Li > Na > K ~ Rb ~ Cs) following

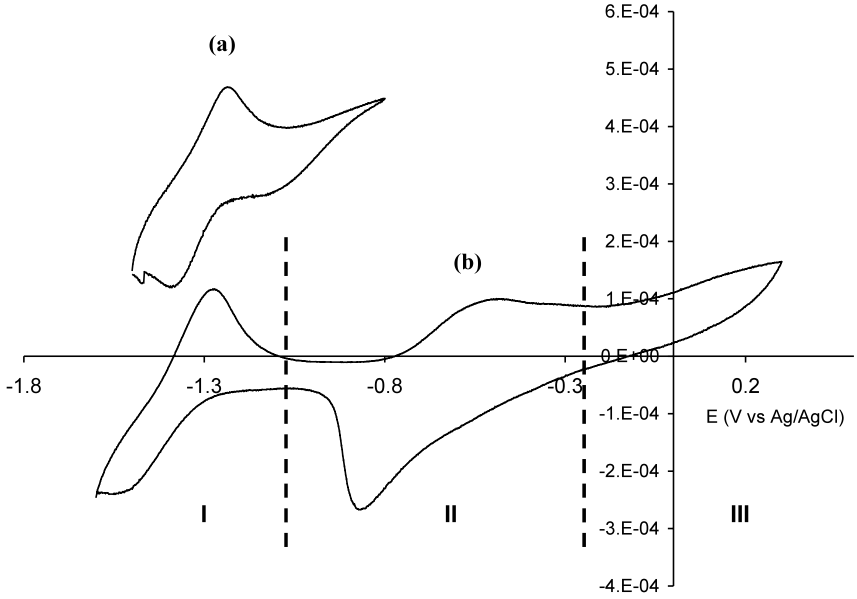

Fig. 1. Typical CVs in aqueous NaCl electrolyte for (a) cobaltabisdicarbollide $[Co(C_2B_9H_{11})_2]^-$ and (b) PPy[Co($C_2B_9H_{11}$)$_2$] obtained with PPy[Co($C_2B_9H_{11}$)$_2$] deposited on glassy carbon electrodes Ø = 3 mm. Electrolyte: NaCl 0.1 M; scan rate of electrode potential 20 mV s^{-1}.

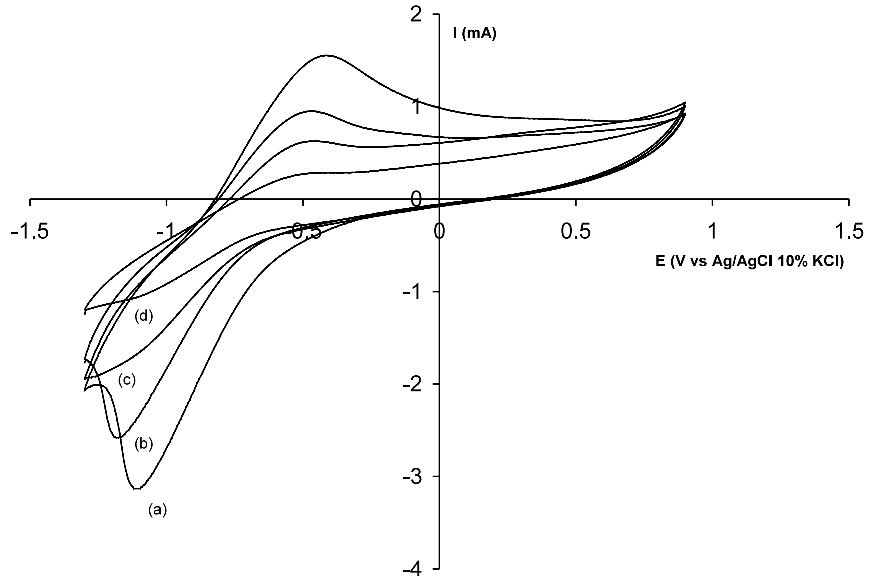

Fig. 2. Cyclic voltammetry in aqueous sodium naftalensulfonate of PPy[$Co(C_2B_9H_{11})_2$] with successive amounts of gelatine: (a) 0%, (b) 1%, (c) 3%, (d) 5%. Scan rate of electrode potential 20 mV s^{-1}.

an opposite sequence according to their ionic volume [24]. This result is easily interpreted considering that the cation capture implies not the naked ions but ions with their hydration sphere. These experiments also provide the possibility of intelligent membrane implementation. The membrane is sensitive to the nature of the ions, therefore, providing a means for selective separation. The reduction potential control will allow us to obtain selective or at least preferential cation capture when the membrane will be reduced in a multi cationic mixture.

Electronic quartz microbalance studies have demonstrated [25–28] that PPy films usually present two distinct processes of ion capture and release depending on the applied potential. In general, cationic exchange is found at more cathodic potentials than the anionic one. The experimental strategy to confirm the possible anionic dependence of the electrochemical process at region III was to limit as much as possible the electrolyte anionic movement inside the polymer using high volume anionic surfactants. Fig. 4a and b shows the CV's corresponding to a PPy[$Co(C_2B_9H_{11})_2$] membrane potentiodynamically cycled in sodium *p*-dodecylbenzenesulfonate and in NaCl, respectively. The curves matching is reasonably good at low potentials (region

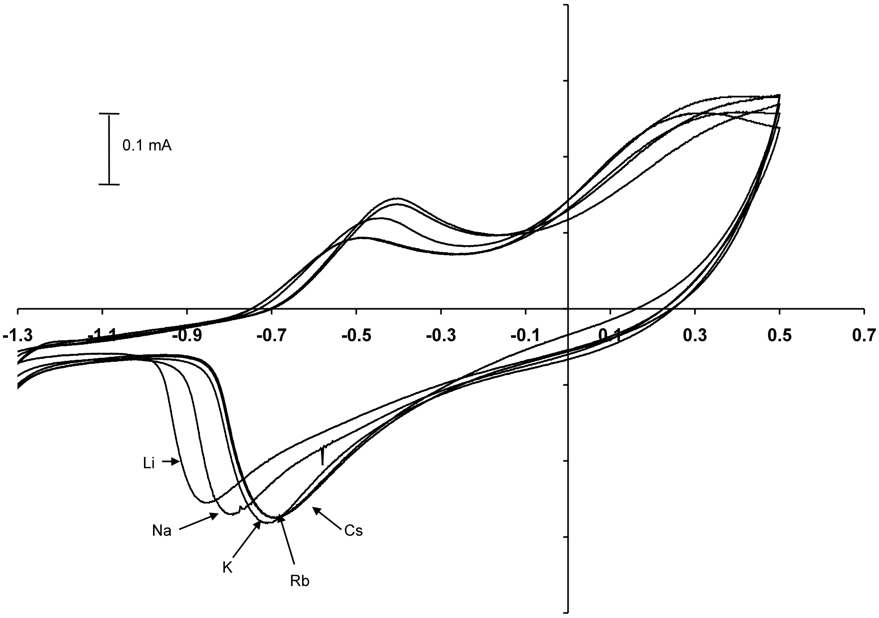

Fig. 3. Cyclic voltammetry of PPy[$Co(C_2B_9H_{11})_2$] in aqueous alkaline chlorides: LiCl 0.1 M, NaCl 0.1 M, KCl 0.1 M, RbCl 0.1 M, CsCl 0.1 M. Scan rate of electrode potential 20 mV s^{-1}.

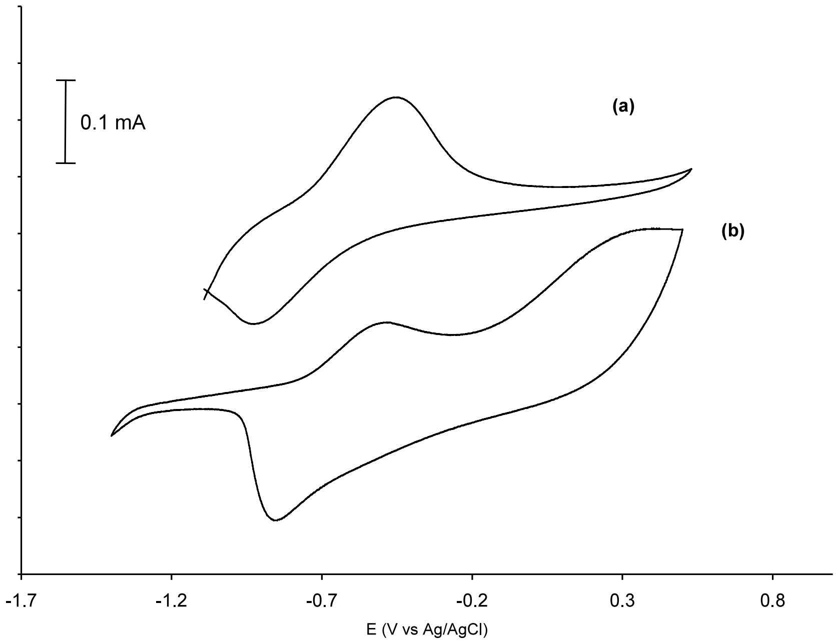

Fig. 4. Cyclic voltammetry at pH 7 of PPy[$Co(C_2B_9H_{11})_2$] in aqueous (a) dodecylbenzenesulfonate and, (b) NaCl at scan rate of electrode potential 20 mV s^{-1}.

II) but clearly inhibits the region III electrochemical process, and therefore, confirms that the process taken place there is due to a minor anionic exchange with the media. It has to be pointed out that no evidence of doping agent leakage is detected during cyclic voltammetry experiments. This fact and the flat response in region III at the firsts scans of cyclic voltammetry indicates that the cobaltabisdicarbollide dopant is not related with this anion exchange.

3.2. Cation uptake measurements

The total cation uptake and the process selectivity was tested by reducing the PPy[$Co(C_2B_9H_{11})_2$] membrane in LiCl, KCl and in LiCl:KCl (1:1) aqueous solutions. After membrane mineralization by acid digestion, Li, Co and K analysis were performed in the resulting solution by flame atomic absorption spectroscopy.

No important differences in the total Co amount were detected between the PPy[$Co(C_2B_9H_{11})_2$] reference membranes (without the reduction treatment) and those measured after the cation uptake measurements. All measurements indicated a Co weight concentration in the membrane around 10%, which corresponds to one cobaltabisdicarbollide unit per four Py rings. This result is in good agreement with our previous results on XPS [21] analysis. It also confirms the electrochemical results indicating that no dopant leakage occurs during the reduction process, and therefore, that the material performs as a true cation exchanger during reduction. Confirming this result, weight measurements before mineralization, indicated that there is no membrane mass decrease due to a possible dopant loss. The Li and K intramembrane concentration in the non reduced membranes was clearly below the method detection limit. This can conclude that the effect of the ions merely fixed by static equilibrium between film and solution is fully negligible and all the measured ionic concentration is due to cation uptake during reduction. As no irreversible dopant loss occurs during the reduction, the K–Co and Li–Co atomic concentration ratios were chosen to quantify the cation uptake capacity of the membrane. Fig. 5 shows the K–Co and Li–Co ratios versus the applied reducing potentials. It can be seen that at low reducing potential small Li–Co and K–Co ratios are measured. At slightly more cathodic potentials these ratios quickly increase to obtain an asymptotic value around 0.6. The behavior at low reducing potentials could be fully explained by comparing the total reduction charge. At the low reducing potentials the intensity is low and the process requires long times to get full reduction. As this is not reached, lower cation uptake was obtained. It seems that there is a threshold near the 60% of possible cation uptake (0.6 value in Li–Co and K–Co ratios) even in highly reducing (−1.5 V) conditions. No parallel and simultaneous process due to other ions uptake/release or dopant liberation can be argued to account for this as the total charge recorded in the process corresponds with the cationic concentration. The 0.6 value in cation efficiency can be explained by the conductivity drop during the reduction process that hinders cation insertion. Low cation uptake efficiency, denoted by low Li–Co and K–Co ratios, is always observed when the total charge do not reach the typical

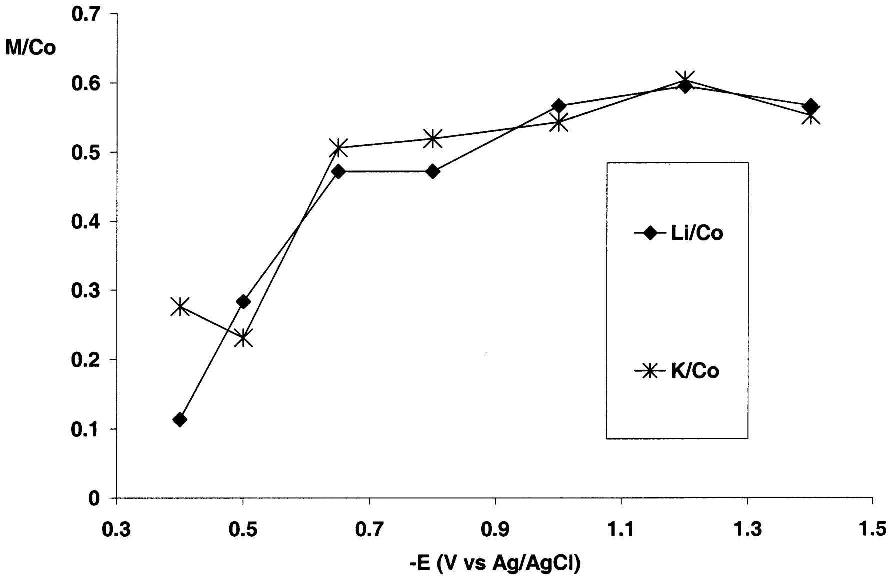

Fig. 5. Li–Co and K–Co ratios of reduced membranes in a mono cationic electrolyte solution.

value of ~200 mC per membrane unit weight (mg), which corresponds to the maximum cation uptake efficiency. As expected, the reduction time necessary to reduce the membrane is clearly affected by the cation nature (Table 1). The t_{90} values (time in seconds to get the 90% of the total measured charge) are always larger for Li than K, confirming that the larger volume reduces the ionic diffusion rate into the polymer, therefore, enlarging the time required to regenerate the polymer.

Fig. 6 shows the results obtained for reductions in a LiCl (0.1 M)+KCl (0.1 M) mixture. The behavior is similar to this found for the monoelectrolyte. Low Li and K concentrations are obtained at low potentials, but as the potentials increase the membrane tends to reach the 0.6 threshold. Note that at high potentials, the combined Li–Co and K–Co ratios are around 0.7. As the solution is simultaneously 0.1 M in LiCl and 0.1 M in KCl there exists a higher total cationic concentration thus providing an easier membrane reduction. Membrane selectivity is clearly evidenced from the Li–K ratio. As it can be seen in Fig. 6 this ratio never overpass 0.72. Even in the worst reduction potential conditions to obtain Li–K selectivity (−1.5 V) the relative amount of Li is just the 41.8% of the atomic concentration of K. An adequate reduction potential selection nicely improves the cation selectivity. Almost 100% selectivity K versus Li is obtained when the reduction potential is under −0.65 V, but as it can be seen in Fig. 6, the selectivity increase produces a substantial decrease in the cation capture efficiency. Charge measurements on Table 1 corroborate that this low cation capture efficiency is due to a non-complete membrane reduction, which could be overlooked by increasing the reduction time.

3.3. *Membrane stability*

Long term membrane stability was checked by monitoring the oxidation and reduction charge versus time after successive charge–discharge cycles (−0.65 and 0 V, respectively). Cation capture by polymer reduction and the subsequent membrane regeneration by reoxidation is an almost 100% reversible process. No

Table 1
Total reduction charge, atomic concentration ratios and reduction time (t_{90}) obtained for some membranes

	E (V)	*Q*/*m* (mC mg^{-1})	Li–Co	K–Co	Li–K	t_{90} (s)
LiCl	−0.5	88.0	0.28	–	–	3436
	−0.8	188.5	0.47	–	–	2577
	−1.4	220.3	0.59	–	–	1242
KCl	−0.5	71.2	–	0.23	–	2507
	−0.8	184.8	–	0.51	–	1205
	−1.4	210.2	–	0.6	–	844
LiCl+KCl	−0.5	66.6	0	0.2	0	2690
	−0.8	153	0.13	0.31	0.41	646
	−1.4	225.6	0.32	0.44	0.72	305

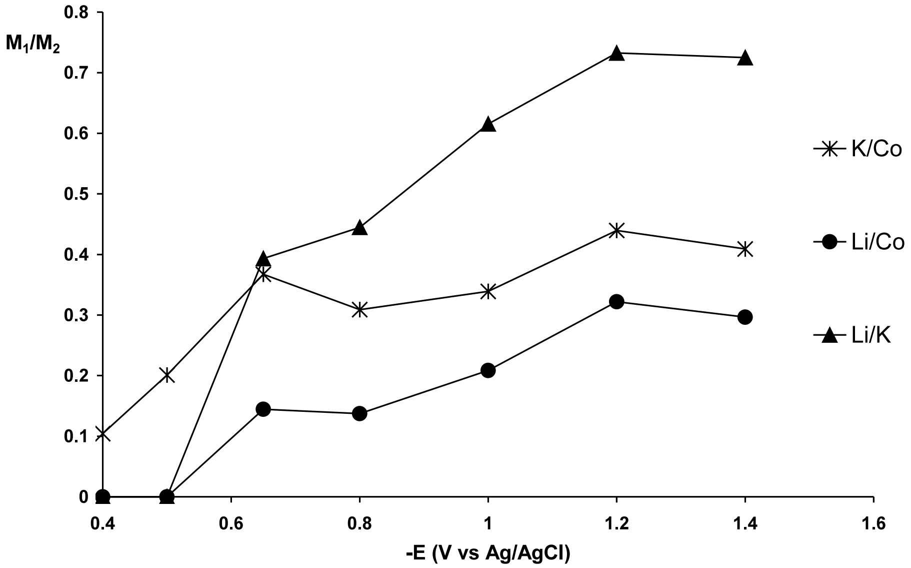

Fig. 6. K–Co, Li–Co ratios for reduced membranes in LiCl 0.1 M + KCl 0.1 M mixture solution. The ▲ graph represents the selectivity of Li cation over K cation.

significant differences in the total charge passed during oxidation and reduction processes (17.3 and 17.5 mC, respectively) were obtained. Even after 40 successive charge–discharge cycles the total charge was reduced in less than 2 mC. This result confirms the absence of degradation processes such as dopant leakage during reduction or conductivity loss due to OH^- attack during oxidation (over oxidation) [29,30] or mechanical degradation associated to volume changes during charge–discharge processes [31–33] that could decrease the operation life of the membrane.

A typical problem during the PPy membranes reoxidation process is the low reoxidation level q_2/q_1 [31]. Ratios q_2/q_1 around 0.5 and 0.3 have been described for sulfate and naftalene-1,5-disulfonate doped PPy membranes, respectively. This effect has been interpreted as an increase in the resistance to diffusion of anions into a film shrunk during reduction process. Reoxidation ratio usually increases ($q_2/q_1 \sim 0.9$) if the electrolyte anion is smaller than the dopant. As our measurements performed in NaCl provided q_2/q_1 ratios around 1, and in order to know the extent of this effect in our membranes, charge–discharge measurements were repeated under the same conditions using the sodium salt of dodecylbenzenesulfonate as electrolyte. No major differences were obtained in the q_2/q_1 ratio, confirming once again that main electrochemical process in the membrane is the cation capture.

Acknowledgements

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