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Characterization of acrylic hydrogels by open circuit potential monitoring

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Abstract

A systematic investigation of acrylic type copolymers was performed for determining their mechanical durability and electrolyte retention, when immersed in various media, including aqueous and organic solutions. Optimization of the chemical and dimensional stability of polymers was possible by electrochemical techniques and swelling/dissolution/evaporation tests. Acrylic acid–acrylonitrile copolymers resistant to aqueous and organic media in a wide pH range have been previously employed in various electrochemical applications, including unconventional reference electrodes. This paper introduces a simple and easy to use system for polymer testing, and highlights the ability of electrochemistry to predict polymer behavior in aqueous and organic solutions. Specially designed gravimetric measurements support the electrochemical characterization of the hydrogel samples. It is shown that open circuit potential against time measurements represent suitable tools for evaluating polymer properties.

1. Introduction

Electrochemistry performed on redox species entrapped in hydrogel films has become popular over the past decade [1–16]. Initial work attempted to record direct electrochemistry of hydrogel-immobilized myoglobin [1], cytochrome c [2], hemoglobin [3], or conventional redox couples [4, 5]. More recent applications of hydrogel electrochemistry span from the investigation of enzyme activity [6, 7] and electrocatalytic activity [8–10] to metal corrosion studies [11], devising electrochromic devices [12], sensors [13–15] and reference electrodes (REs) [16–18].

Out of the above examples we describe here two applications relevant to our work. Lu et al. [6] investigated the direct voltammetry and electrocatalytic properties of catalase in polyacrylamide (PAM) hydrogel film casts on pyrolytic graphite (PG) electrodes. Electron transfer between catalase and PG electrodes was greatly facilitated in the PAM film microenvironment. Pishko and coworkers [7] investigated nanocomposite hydrogel thin films consisting of alternating layers of an organometallic redox polymer and oxidoreductase enzymes by electrochemical techniques. Mass transfer, changes in film structure with electrode potential, and substrate dependent current upon addition of enzyme to the multilayer structure, were monitored in real time.

Out of the wide range of electrochemical techniques employed for quality assessment, open circuit potential vs. time (OCP) measurement has recently proven an efficient tool for the study of strongly adsorbing neutral species (CO or I_2) and ions (I^-)[19], in the evaluation of biologically catalysed metal corrosion [20], for the monitoring of microbial biofilm formation in aqueous systems [21], and for the examination of spontaneous processes of polypyrrole (PPy) films in electrolyte solutions, such as polymer redox capacitance discharging and its influence on OCPs [22]. Results of the latter experiments are helpful in the evaluation of polymer charge stability. They are also of significance in the explanation of the dependence of OCP of PPy on the concentration of solution components, which is important for analytical applications of conducting polymers [22].

The use of OCP to evaluate the durability of coatings and polymer films [23] is closely related to our work. Such measurements can be performed in significantly shorter times than those needed to complete long-term exposure tests. Replicate samples and OCP monitoring can be used to develop accurate estimations of the durability of polymer films, coatings, or metal coatings. One can use OCP monitoring as the analytical technique for the characterization of the key structural element of

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our recently described miniaturized reference electrodes (MREs), namely their hydrogel matrix [16, 17, 24]. In this paper we report characterization/optimization studies performed on acrylic acid–acrylonitrile hydrogels, which enable the preparation of copolymers that can serve as dimensionally stable matrices, capable of entrapping supporting electrolytes, with minimum loss of salts into the solution in contact with the hydrogel. This paper introduces a simple and easy to use system for polymer testing, and highlights the ability of electrochemistry to predict polymer behaviour in aqueous and organic solutions. Measurements performed by specially designed gravimetric methods support the electrochemical characterization of the hydrogel samples. It is shown that OCP measurements represent a suitable tool for evaluating polymer properties of interest.

2. Experimental details

2.1. *Materials*

All chemicals were purchased from Aldrich (Milwaukee, WI), unless indicated otherwise. Gel-type electrolyte formulations typically included one or two acrylic monomers: acrylic acid (AA) and acrylonitrile (AN), deionized water (DW), supporting electrolyte (an inorganic salt, preferentially KCl, or quaternary ammonium salt, QAS), photoinitiator, crosslinker, plasticizer (optional), and a thickener (optional). The tested acrylic monomers were AA (99%), AN (99.9%), and 2-(acryloyloxy)-ethyltrimethylammonium chloride (AQA, 72% aqueous solution, Lancaster, Pelham, NH); supporting electrolytes were typically KCl (Spectro pure reagent, SPEX Industries, Inc.), NaCl (>99%) or tetramethylammonium chloride (NMe_4Cl, >99%, Spectrum Quality Products, Inc.); plasticizers were: glycerol (G; >99%, Acros) or ethylenegylcol (99+%, Acros), the photoinitiator was Darocur® 1173 (D), that is, 2-hydroxy-2-methyl-1-phenyl-1-propanone (Ciba Specialty Chemicals, Tarrytown, NY), the crosslinker was *N*,*N′*-methylenebisacrylamide (MBA; 99%, Aldrich), while the thickener was Superfloc N-300 LMW Flocculant, a polyacrylamide (PAA; CYTEC Industries Inc., West Paterson, NJ). DW (18 MΩ cm) was obtained with a Milli-Q™ Water System (Millipore). All organic solvents used were dried and stored over molecular sieves or calcium chloride [25].

2.2. *Preparation protocol*

Hydrogel-type electrolytes were prepared according to a generic recipe, which includes two acrylic monomers, DW, supporting electrolyte (QAS), photoinitiator, and cross-linker. Use of Me_4NCl as the supporting electrolyte was reported previously in literature [26, 27]. The most stable MREs were obtained with hydrogels that contained 26.3 wt % of Me_4NCl. A detailed example of preparing these hydrogels was reported elsewhere [16, 17]. The composition (wt%) of the best mixture (designated 15 in Table 1) is: QAS 26.3; AA 20.3; AN 19.4; DW 30.7; MBA 0.40; and Darocur® 2.9 [28].

For optimizing the polymer composition it was attempted to bring the QAS/AA molar ratio as close to the unit as possible [16, 17]. The interactions between the quaternary ammonium ions and the carboxylic acid groups of AA groups are thought to allow for a better entrapping of QAS in the polymer matrix. It was not possible to attain ratios above 0.85, given that any additional QAS would have caused the final co-monomer mixture to separate into two distinct phases [29], resulting in an unstable electrode potential.

2.3. *Electrochemical measurements*

Electrochemical measurements were performed with a model 660 electrochemical workstation (CH Instruments, CHI, Austin, TX), the undivided glass cell being shielded in a Faraday cage. In the applications described below such hydrogel type REs were referenced to commercial REs: a double junction Ag/AgCl, sat. KCl (DJRE, model 6.0726.100, Ω Metrohm, Herisau, Germany) or a model CHI 111 Ag/AgCl, 3 mol L^{-1} KCl (CH Instruments), in aqueous solutions.

2.4. *Gravimetric measurements*

Swelling/dissolution and dissolution/evaporation tests were performed on hydrogels samples enclosed in an Eppendorf® 20 μL Ultra Micro Tip (Brinkmann Instruments, Inc., Westbury, NY; set-up not shown). The polymer volume was 10 μL, while the surface of the contact area between the sample and the solution was 0.4 mm^2.

The mass of the polymer samples was of ~11 mg; the error on the analytical balance is ± 0.2 mg, which is approximately ± 2 wt% of the polymer mass.

After being immersed in various aqueous an organic media for 10 days, the polymer samples were dried in a desiccator to assess the amount of polymer dissolved in each solution or the amount of liquid was adsorbed by the polymer matrix. Our calculations took into account the weight loss of the polymer sample by drying/evaporation (over 10 days in a desiccator), when not exposed to any solvent.

3. Results and discussion

Ideally, hydrogel-based electrolytes should be chemically inert, dimensionally stable, should not release their salt content into surroundings, and should not be contaminated by the media to which they are exposed to. For hydrogel-based electrochemical applications, such as the manufacturing REs for corrosion studies in hydrogels it is essential to optimize the composition of the polymer matrix. Preliminary work was performed on polymer samples included in larger electrodes (noted as

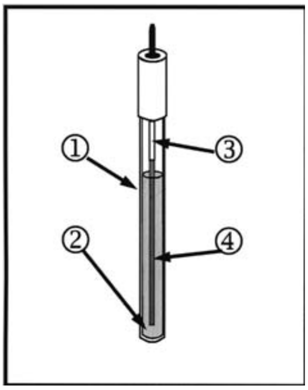

Fig. 1. Set-up for the electrochemical testing of polymers: (1) glass body; (2) polymer matrix; (3) IRE (Ag wire); (4) AgCl coating layer.

NRs), manufactured at 1–5 mL scale, while our research was focused on finding an optimal composition for the polymer matrix, rather than the miniaturization of hydrogel-based systems. NRs represented a step forward in developing an all-solid state RE [30].

The geometry of NRs is similar to the commercially available Ag/AgCl micro-REs [31], but NRs do not contain a porous plug (Figure 1). The electrode consists of a glass tube (*1*; inner diameter 4 mm, length 4–5 cm); an internal reference elements (IRE) (a Ag wire, *3*, coated with a layer of AgCl, *4*) [16]; the polymer matrix (*2*) with entrapped electrolyte, which rises in the glass body to ~3.5 cm, and typically corresponds to a polymer volume of 1.5–2.0 mL [30]. This design allows for maintaining the IRE in an environment of constant Cl^- concentration, with the anion incorporated in the hydrogel (i.e., entrapped in the polymer matrix). This acrylic hydrogel contains an inorganic salt, such as KCl or NaCl, or an organic salt [18], which serve as the Cl^- supply of the polymer matrix. By its special composition the hydrogel should retain both anions and cations. Leaching of cations from the polymer matrix was studied previously via atomic absorption spectroscopy for Na^+ (results being applicable to K^+, as well) and ICP-MS for Ag^+ [16,17]. It was shown that the hydrogel entraps cations and prevents contamination of the analyte.

Various compositions of the hydrogel were tested for dimensional stability by direct immersion in solvents and as an element of NRs. Table 1 lists the most relevant qualitative compositions.

3.1. *Testing the chemical and dimensional stability of hydrogels in NR systems*

As part of an NR system, a chemically and dimensionally stable hydrogel should generate a constant and reproducible potential value, which remains unaffected by the composition of the solution in which NR is immersed [32]. For Ag/AgCl-based NRs, the stability of the potential depends on the ability to maintain a constant Cl^- concentration (activity) around the IRE. The Nernst equation describes the electrode potential as follows:

$$E_{\mathrm{Ag/AgCl}} = E^0_{\mathrm{Ag/AgCl}} - \frac{RT}{F}\ln a_{Cl^-} \tag{1}$$

When the IRE is contained in a polymer matrix, the stability of the electrode potential depends on the properties of the polymer matrix, namely its ability to retain Cl^- ions without leaching or absorbing them from the analyte. We have found that Cl^--entrapping properties of the polymer matrix can be inferred from OCP measurements, a technique which, consequently, represents an important method for the evaluation of the polymer composition and its chemical stability. Another test performed on various polymer matrices monitored their dimensional stability; if swelling or shrinking of the matrix was noticed during measurements for a particular composition, then the polymer was deemed to be unfit.

3.1.1. *Testing of hydrogel components: supporting electrolytes*

It has been demonstrated by OCP measurements that KCl is a better supporting electrolyte than KBr or NaCl

Table 1. Representative polymer compositions of NRs

Composition	Polymer composition	Number of electrodes tested	Main problem associated with NRs
1	AA, D, DW, PAA, G, KBr	3	unstable potential
2	AA, MBA, D, DW, PAA, G, KCl, NaH_2PO_4	3	unstable potential
3	AA, D, DW, PAA, G, KCl	4	swelling
4	AA, MBA, D, DW, PAA, G, KCl, NaCl	4	unstable potential
5	AA, MBA, D, DW, PAA, G, KCl	5	Cl^- sensitivity
6	AA, MBA, D, DW, PAA, G, NaCl	4	unstable potential
7	AA, MBA, D, DW, G, KCl	5	Cl^- sensitivity
8	AA, MBA, D, DW, PAA, KCl	5	Cl^- sensitivity
9	AA, MBA, D, DW, KCl	5	Cl^- sensitivity
10	AQA, MBA, D, DW, G	2	swelling
11	AQA, MBA, D, DW	2	swelling
12	AA, AN, MBA, D, DW, NBu_4BF_4	4	shrinking
13	AA, AN, MBA, D, NBu_4BF_4	4	non-reproducible
14	AA, AN, MBA, D, DW, KCl	12	Cl^- sensitivity
15	AA, AN, MBA, D, DW, NMe_4Cl	37	–

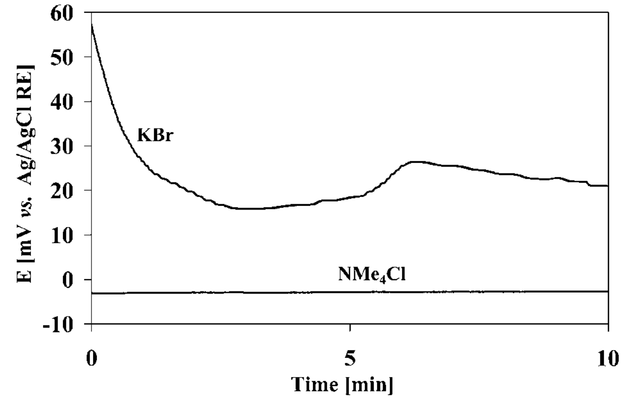

Fig. 2. OCP of NRs for compositions 1 (supporting electrolyte: KBr) and 15 (supporting electrolyte: NMe_4Cl) vs Ag/AgCl RE, in NaCl 0.9%.

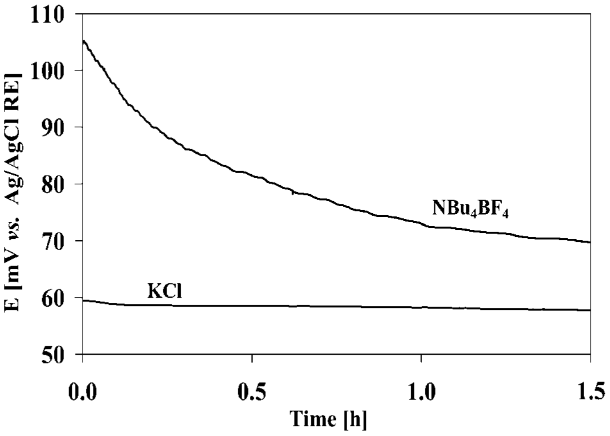

Fig. 3. OCP of NRs for compositions 14 (supporting electrolyte: KCl) and 12 (supporting electrolyte: NBu_4BF_4) vs Ag/AgCl RE, in NaCl 2.0%.

(not shown). During polymerization, KBr and NaCl often disrupted the homogeneity of the matrix, yielding eventually distinct phases; as a result, electrode potentials recorded in OCP became unstable over time. Potassium chloride, however, was deemed excessively susceptible to leaching out of the matrix, likely due to the relatively small ionic radii of its ions. A QAS (e.g., tetrabutyl ammonium bromide or NMe_4Cl) was used instead KCl, with the idea that the more bulky cation would be better retained by the polymer matrix, delaying the loss of ions from the hydrogel. By using OCP monitoring it was found that electrodes based on NMe_4Cl had an improved long-term potential stability as opposed to KCl-based NRs. Figure 2 in which OCP curves are compared for electrodes of compositions 1 and 15 (Table 1), indicates a much greater stability for the polymer matrix containing NMe_4Cl relative to KBr. Thus, OCP curves reveal the effect of different salts on the ability of hydrogels to sustain a stable potential value of IRE.

The use of a bulkier QAS associated with a bulky anion was explored, with the hope that loss of ions would be reduced further. Therefore, tetrabutyl ammonium tetrafluoroborate (NBu_4BF_4) was chosen as the supporting electrolyte. It was found that the incorporation of NBu_4BF_4 into the polymer matrix (with no other modifications) resulted in a significant volume shrinkage (by ~30%) of the polymer, and this dimensional change was also manifested in an unstable electrode potential. Figure 3 displays OCP curves recorded with electrodes containing hydrogels 12 and 14 (Table 1). Formulations with KCl supporting electrolyte show a better potential stability as compared to NBu_4BF_4. When NBu_4BF_4 was added to the comonomer mixture under crystalline form, the dimensional stability of NR improved significantly (volume shrinking <10%), and the obtained potential was stable (with variations of less than ±0.1 mV over 2 h; not shown). Unfortunately, the potential generated by these hydrogels varied from one batch to another; therefore, they were rated as unsatisfactory for electrochemical applications.

It was found by OCP investigations in solutions of various Cl^- concentrations that composition 14 yielded NRs and MREs with Cl^- sensitivities 10 times greater than that obtained for composition 15. Hence, as the result of OCP monitoring of various hydrogels it was concluded that out of the examples listed in Table 1, composition 15 had the best chemical stability.

3.2. *Gravimetric tests of hydrogels: optimal composition and dimensional stability*

To confirm results obtained by OCP measurements in identifying the optimal composition of the polymer that confers the greatest chemical and dimensional stability, we performed a series of gravimetric tests on various polymerized samples. Gravimetric measurements included swelling/dissolution, dissolution/evaporation, and drying tests. They were called to prove the optimal composition and physico-mechanical properties of the polymer matrix, such that they: (a) show dimensional stability, that is, low extent of swelling and/or dissolution in aqueous salt solutions and in organic media, and (b) retain the incorporated salt over a long time period, when exposed to various chemical environments, that is, the leaching of ions is minimized.

Gravimetric tests verified the OCP measurements in that the most mechanically stable and chemically inert hydrogel matrices were obtained with an AA/AN monomer molar ratio of 1.0/1.3 and a cross-linker content of 0.40 wt %. For swelling/dissolution curves in Figure 4 there is almost no variation of the mass outside the range of 98–102 wt % for MeOH, PC, acetonitrile (ACN), and MC (not shown, but similar in trend to PC). In 0.2 mol L^{-1} KCl solution in DW, DW, and EtOH there is a mass increase by ~10 wt %. (DW and EtOH not shown on the graph, but they exhibit similar behaviour to the 0.2 mol L^{-1} KCl solution in DW.) Except for PC, in which polymer swelling was more pronounced than its dissolution (8 wt % overall mass gain for 10 days

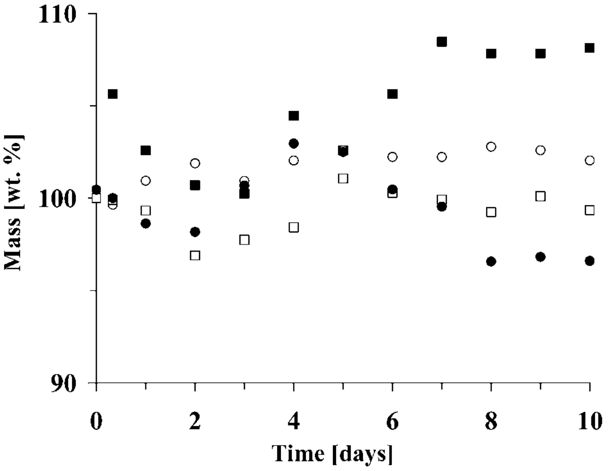

Fig. 4. Swelling/dissolution curves of AA/AN (1.0/1.3 molar ratio) copolymer, composition 15. Solvents are: (■) 0.2 mol L^{-1} KCl in deionized water (similar in trend to deionized water and ethanol), (□) propylene carbonate (similar in trend to methylene chloride), (●) acetonitrile, (○) methanol.

immersion), dissolution overcame the swelling; the weight loss decreased in the order of decreasing the polarity of the solvents, which is in accord with the findings of the dissolution/evaporation tests [29]: DW (27 wt %) ≈ KCl 0.2 mol L^{-1} (25 wt %) > MeOH (22 wt %) > EtOH (12 wt %) > ACN (8 wt %) > MC (1 wt %). These results typically correlate with OCP measurements (not shown).

3.2.1. *Determination of the pH range of stability*

A gravimetric study was performed on polymer samples with an Eppendorf tip set-up similar to the one in Fig. 1, [16], without IRE (result not shown). The pH stability range was also investigated by OCP monitoring. Over the pH range from 1 to 12 the mass change of the polymer matrix was within ±5 wt %, allowing for the use of the polymer over periods up to 10 days. At pH 13, however, the polymer samples exhibit considerable swelling (25 wt %), therefore this pH value sets an upper limit for the use of MREs (electrodes can be employed in solutions of pH 13 for just a few hours).

3.3. *Testing the effects of cross-linking on potential stability*

OCP measurements combined with gravimetric methods were useful in establishing the optimal degree of cross-linking of the polymer. Appropriate cross-linking is necessary for the polymer matrix to maintain its structural integrity in a variety of media. Experiments were performed to assess whether increasing the cross-linking concentration would improve the performance of the polymer, since the degree of cross-linking in the polymer (directly related to the concentration of the cross-linking agent in the monomer composition) determines to a significant extent the internal geometry (e.g., the spacing between polymer chains in the matrix) and the solvent resistance of the polymer [33]. As preliminary tests swelling/dissolution studies were utilized, and mass change was recorded over time (up to 45 days) for samples immersed in aqueous solutions or organic solvents. Out of three polymer compositions: 15 (which contains 0.40% MBA), 15a (0.44% MBA, 10% more than 15) and 15b (0.50% MBA, 25% more than 15), 15 showed the most uniform response in all tested media, hence it appears as the best choice.

Again, OCP measurements have proven extremely useful for the determination of the chemical stability of hydrogels having various degrees of cross linking. For performing the electrochemical tests, MREs were assembled containing polymer compositions 15, 15b, and 15c, and their behaviour as reference half-cells was monitored. After polymerization, the polymer matrices obtained from compositions 15a and 15b became opaque and white to yellow-brown in colour, as opposed to colourless and transparent for composition 15. When tested, compositions 15a and 15b demonstrated instabilities which precluded them from further use. Assembled MREs were placed in 3 mol L^{-1} KCl, and measured against DJRE (Ag/AgCl, also 3 mol L^{-1}). Results are displayed in Figure 5 for MREs containing as IREs stainless steel wires [24, 29]. The plot for composition 15a shows a 600 mV drift over ~20 h. Even after the potential levels off slightly (~5 h), there are still deviations greater than 50 mV over the remainder of the experiment. Composition 15b also shows potential instability, with a drift of over 150 mV, the scan being associated with erratic potential peaks. The curve for composition 15 presents a standard deviation of only 1.14 mV over 14 h, indicating that this polymer is the most stable, and represents the best choice for the construction of reference half cells.

To asses that these results are not linked to the type of IRE used inside the MRE, several other IREs were employed, that is, Ag/Ag_iX IREs. OCP curves displayed

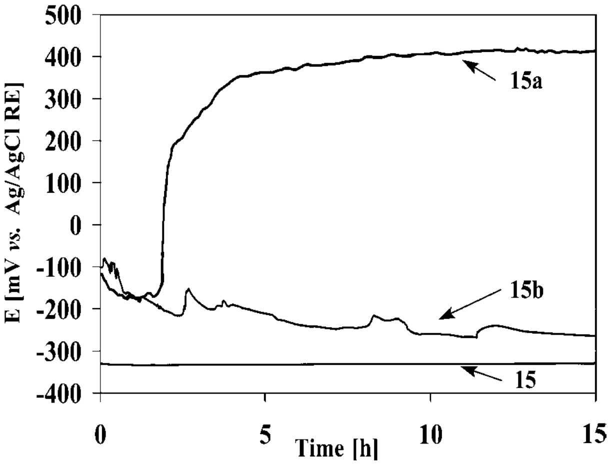

Fig. 5. OCP for MREs based on AA/AN (1.0/1.4 molar ratio) copolymer, with various degrees of cross-linking; IRE is stainless steel wire.

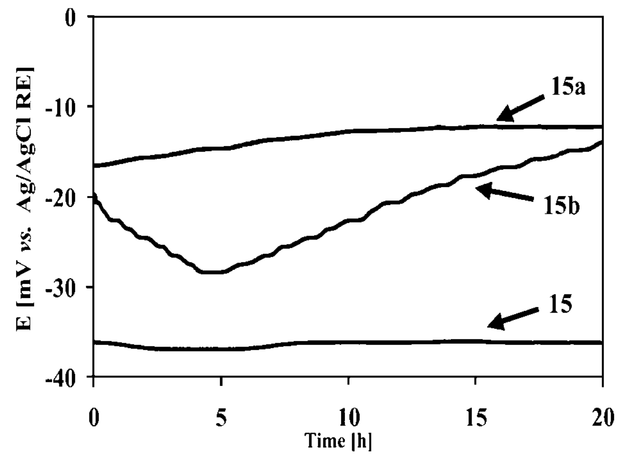

Fig. 6. OCP for MREs based on AA/AN (1.0/1.3 molar ratio) copolymer, with various degrees of cross-linking; IRE is Ag/AgSCN.

in Figure 6 were obtained with electrodes based on Ag/AgSCN IREs [28]. When immersed in KCl 3 mol L^{-1} composition 15 shows stability of the electrode potential within ± 0.5 mV, composition 15a indicates a variation of the electrode potential of about ± 2.5 mV, while further increase of the MBA content (composition 15b) results in a less stable electrode potential (±6.5 mV). It should be noted here that for cross-linker concentrations below 0.40% the polymer underwent significant swelling (>25%) and lacked dimensional stability [33].

4. Conclusions

Open circuit potential against time measurements have proven an appropriate technique for the evaluation of the composition and functionality of various hydrogels, including their chemical and dimensional stability. Results of gravimetric measurements supported the electrochemical characterization of the hydrogel samples. These investigations resulted in the development of a hydrogel appropriate for being used as a polymer electrolyte for miniaturized reference electrodes and in corrosion studies.

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