JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) · SHORT COMMUNICATION

SHORT COMMUNICATION

Electrogeneration of acrylamide-bisacrylamide gel films on platinum

T. F. OTERO, F. GARCÍA

Universidad del País Vasco, Facultad de Química, Departamento de Ciencia y Tecnología de Polímeros, Laboratorio de Electroquímica. Apdo. 1072, 20080 San Sebastián. Spain

C. DANILOWICZ y E. CALVO

INQUIMAE, Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales. Pabellón 2, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Received 18 June 1993; revised 28 September 1993

1. Introduction

Hydrogels based on polyacrylamide are crosslinked networks of polymer swollen with water with good chemical and mechanical stability and resistance to microbial degradation. They have been extensively used as electrophoresis media and as support to immobilize enzymes or redox proteins [1, 2]. Electrodes modified with catalysts supported on electrochemically generated polymers offer the advantage of automatic deposition in a one-step operation with control of growth, adherence and thickness.

Electropolymerization of vinyl polymers in solution has been extensively studied under different experimental conditions. However, most of the work has dealt with the production of polymer in solution [3, 5]. Anodic polymerization in solution is accomplished in the presence of acrylamide in organic solvents such as DMF [6, 7] or in aqueous solutions at iridium oxide [8, 9] and platinum [10].

Electroinitiation of soluble acrylic polymers is characterized by the presence of an induction time that has been related to the simultaneous oxidation of monomer, solvent and support electrolyte [11]. Under certain conditions formation of insoluble gel deposits at the anode has been observed [6].

The purpose of this work is to study the conditions under which a nonsoluble crosslinked copolymer of acrylamide and bisacrylamide deposits on platinum electrodes. The effect of electrode potential and concentrations of acrylamide, bisacrylamide and nitrate was investigated.

2. Experimental details

Electrochemical polymerization was carried out potentiostatically in a conventional three-electrode cell with a thermostating water jacket. A 1 cm^2 platinum plate electrode in the vertical position was employed as working electrode.

Acrylamide and N,N′-methylenebisacrylamide (Merck) and sodium nitrate were used without further purification. Ultrapure water from Milli-pore Milli-Q reagent water system was employed. The unbuffered aqueous solutions were purged with argon.

A PAR M273 poteniostat/galvanostat was employed and the electrical charge was calculated by integration of the chronoamperometric curves after poteniostatic steps applied to the working electrode. A saturated calomel electrode (SCE) was used as reference and potentials are quoted with respect to it.

Film growth was followed by weighing the electrode after each experiment using a Sartorius 4504 MPS ultramicrobalance (10^{-7} g sensitivity). The electrode was previously dried in methanol, allowed to equilibrate with atmospheric humidity and weighed. The electrode weight was taken as a relative measure of the hydrogel film thickness. The presence of soluble polymer in solution was verified by precipitation in dried methanol at 5 °C.

3. Results and discussion

Figure 1 shows that acrylamide and bisacrylamide are electroactive above 1.5 V with simultaneous oxygen evolution. Oxygen overvoltage is enhanced in the presence of acrylic monomers. Gradually a hydrogel layer grows on the electrode, and the current efficiency for the oxidation of water decreases. Acidification of the solution adjacent to the electrode is expected from oxygen evolution simultaneous to the polymer formation [10]. This was verified by Bromocresol green.

Film formation was evaluated by ultramicrogravimetry and the total electrical charge consumed at the electrode was studied as a function of electrode potential, acrylamide and nitrate concentrations as shown in Figs 2, 3 and 4, respectively.

Charge increases with electrode potential and nitrate concentration (Fig. 2 and Fig. 4), while a decrease in charge is apparent upon increasing the monomer concentration (Fig. 3). This latter effect can be interpreted as due to autoinhibition by electrode processes that involve acrylamide.

Polymer film weight shows maxima in all three figures and for constant monomer and nitrate concentrations the rate of film growth also shows a maximum for a particular concentration of bisacrylamide (Fig. 5). These results are indicative of the existence of optimal experimental conditions for the formation of an adherent poly-(acrylamide–bisacrylamide) layer on platinum; and the presence of complex electrode kinetics with more than one competing anodic process during film growth. At higher potentials oxygen evolution is considerable and films grown under such conditions are poorly adherent, falling

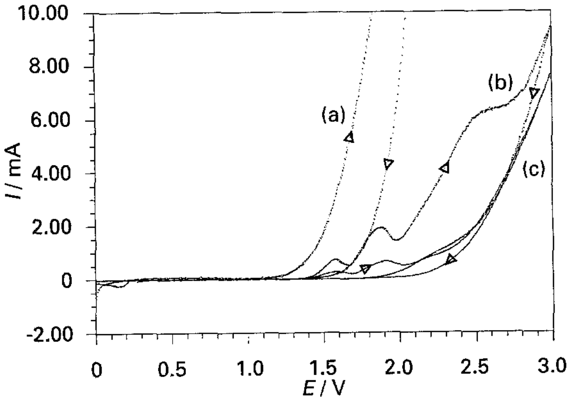

Fig. 1. Cyclic voltammetry at a platinum wire electrode in: (a) 0.3 M $NaNO_3$; (b) 0.16 M Bisacrylamide and 0.3 M $NaNO_3$; (c) 4 M acrylamide and 0.3 M $NaNO_3$. Sweep rate: 0.05 V s^{-1}, Temp.: 35 °C.

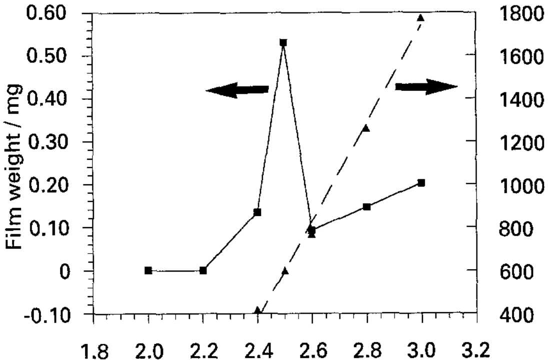

Fig. 2. Electrical charge consumed and weight of the grafted film obtained by polarization of a 1 cm^2 platinum electrode in 4 M acrylamide, 0.16 M bisacrylamide and 0.3 M $NaNO_3$ aqueous solution for 30 s at 35 °C and different anodic potentials (vs SCE).

off the electrode when dried in methanol. In addition to the formation of an insoluble film on the electrode, soluble polymer is also formed during electropolymerization since precipitate is obtained when the remaining electrolysis solution is treated with an excess of methanol.

Under the experimental conditions employed anodic electrode reactions are expected to initiate a free radical chain polymerization in solution [12]. It should be noted that hydrogel film weight also increases with nitrate concentration with a maximum at 0.3 M in Fig. 4; thus nitrate must be involved in the formation of insoluble polymer on the electrode. Nitrate has been found to participate in the electropolymerization of acrylamide in DMF [6] and acrylic acid-acrylamide copolymer in aqueous solutions [12].

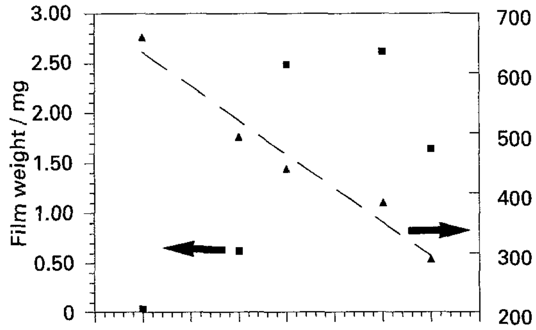

Fig. 3. Charge consumed and weight of the grafted polymer to a 1 cm^2 platinum electrode polarised for 30 s in different acrylamide concentrations 0.16 M bisacrylamide and 0.3 M $NaNO_3$ aqueous solutions at 35 °C.

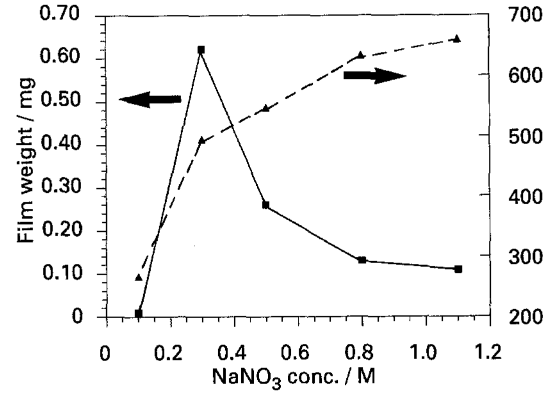

Fig. 4. Film growth and consumed charge at different electrolyte concentrations in 4 M acrylamide and 0.16 M bisacrylamide, $E_{\text{applied}} = 2.5$ V during 30 s at 35 °C.

Bis-acrylamide seems to promote the film insolubility, favouring reactions between polymeric chains as expected: the larger its concentration the larger the fraction of cross linked polymer on the electrode with respect to soluble polymer. However, the maximum film weight at 0.16 M bisacrylamide is difficult to rationalize, unless for higher concentrations of bisacrylamide nonadherent films result and drop off the electrode. This has been confirmed by the finding of insoluble polymer at the bottom of the cell for high concentrations of bisacrylamide. In the formation of the gel layer, free radicals generated by electrode reactions diffuse outwards and react with incoming monomer molecules towards the electrode. The film grows through a moving boundary where free radicals meet monomer molecules and this boundary extends towards the solution with time. Soluble oligomers and linear polymer on the other hand, diffuse outside into the solution. Figure 5 shows that the hydrogel film weight increases linearly with time at constant potential. This has also been observed for acrylic acid-acrylamide copolymer [12] and indicates that film growth has no diffusion limitation.

The hydrogel layer is not a barrier to diffusion since

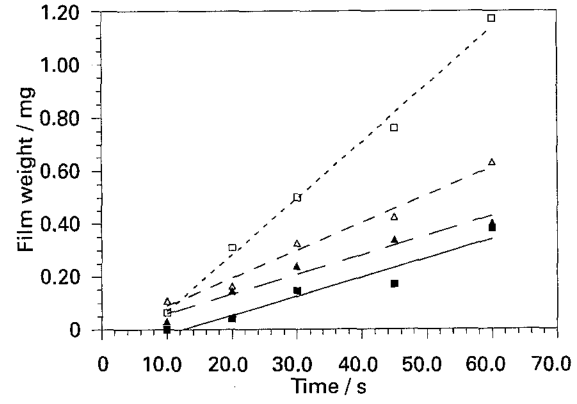

Fig. 5. Film growth for increasing bisacrylamide concentrations: (■) 0.12 M, (□) 0.16 M, (△) 0.2 M, (▲) 0.25 M in 4 M acrylamide and 0.3 M $NaNO_3$, $E = 2.5$ V during 30 s at 35 °C.

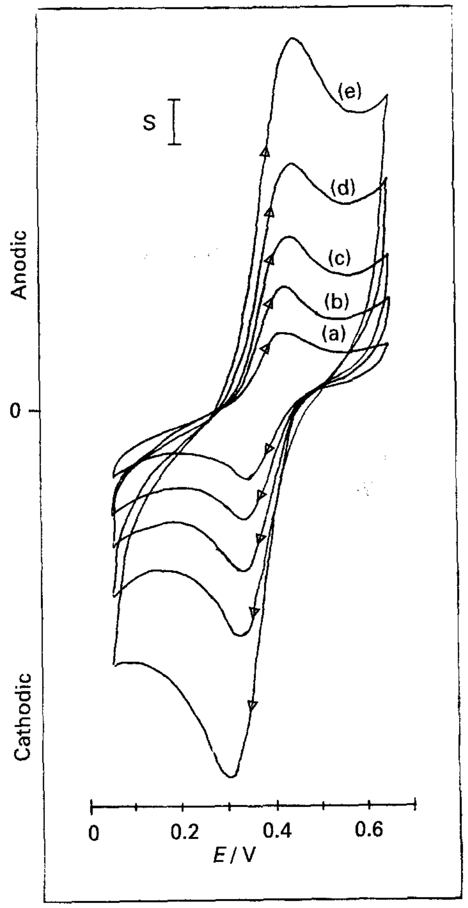

Fig. 6. Current potential curve at 1.04 mM ferrocene monosulphonate at the platinum electrode covered with crosslinked acrylamide hydrogel in 0.1 M $NaNO_3$. Scan rate: (a) 0.02, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.5 V s^{-1}. $S = 0.01$ mA.

there is no appreciable difference in the cyclic voltammetry of a solution of ferrocene monosulphonate at a polymer coated electrode and at bare platinum (Fig. 6), with a diffusion coefficient that is only 50% lower in the former case.

It should be noted that low local pH and vigorous gas evolution at extreme positive potential would prevent the use of this electropolymerization method with active biological materials. Milder conditions of electrochemical polymerization should be found. However, the results presented show the feasibility of carrying out electropolymerization of crosslinked acrylic hydrogels in aqueous solution.

Acknowledgements

Financial support of the program 'Amerika eta Euskaldunak' from the Basque Government, of ICI (Spain), CONICET (Argentina) and University of Buenos Aires is greatly appreciated.

References

[1] K. Mosbach (ed.), 'Methods in Enzymology', Vol. 44 (1976) p. 54.
[2] R. Harland and R. Prod'homme (eds), 'Polyelectrolyte Gels: Properties, Preparation and Applications', ACS Symposium Series 480, American Chemical Society (1992).
[3] T. F. Otero and M. A. Mugarza, *Makromol. Chem.* **188** (1987) 2885.
[4] S. N. Bhadani and Y. K. Prasad, *ibid.* **178** (1978) 1841.
[5] T. F. Balasubramanian and V. Mahadeva, *J. Polym. Sci.* **27** (1989) 2685.
[6] T. F. Otero and A. Marijuán, *J. Electroanal. Chem.* **304** (1991) 153.
[7] S. J. Bhadani, Y. K. Prasad and S. Kundu, *J. Polym. Sci.* **18** (1980) 1459.
[8] T. F. Otero, *Makromol. Chem., Rapid Commun.* **5** (1984) 125.
[9] T. F. Otero, M. S. Larrocha and E. de Larreta, *B. Electrochem.* 4(7) (1988) 659.
[10] S. N. Bhadani and Y. K. Prasad, *Polymer Letters Ed.* **15** (1977) 721.
[11] T. F. Otero and F. García, *Electrochim. Acta* **37** (1992) 1083.
[12] T. F. Otero and J. M. Sarasola, *J. Electroanal. Chem.* **256** (1988) 433.