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An ac impedance study of the fractal geometry of silver films electrodeposited within a polymer matrix

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Silver films ($\sim 10^{-6}$ m) have been electrodeposited within a polymer matrix ($\sim 10^{-5}$ m) of poly-vinylidene fluoride trifluoroethylene copolymer 60–40 cast on the surface of a stainless steel electrode. It is shown that the fractal geometry of the polymer–metal interface, which is not open to direct observation, can be characterized by means of ac impedance measurements made on the electrode in acetonitrile solution.

1. Introduction

The seemingly complex problem of the description and mathematical modelling of the interface between a rough electrode and an electrolyte solution has been illuminated by the fractal geometry of Mandlebrot [1]. Such boundaries have been studied using ac impedance techniques and it has been suggested [2–6] that a rough electrode of fractal dimension D ($2 < D < 3$) shows a constant phase angle admittance of

$$Z^{-1} = A(\mathrm{j}w)^{\alpha} \quad (1)$$

where A is a frequency independent real constant, w is the frequency and $\mathrm{j} = (-1)^{1/2}$. The exponent $\alpha = (D - 1)^{-1}$ [2–6] and it can be appreciated that $D = 2$ generates the purely capacitative behaviour associated with a perfectly smooth surface, whereas $D = 3$ corresponds to $\alpha = \frac{1}{2}$, which is a result previously deduced for the limiting case of a porous elecrode [7, 8]. The problems of surface diffusion on, and cyclic voltammetry and chronoamperometry at, fractal electrodes have also been considered [9, 10].

In this paper we use ac impedance data to characterise the geometry of silver films grown within a polymer matrix. Films are metallized using non-aqueous electrochemical techniques in which the solvent system is suitably chosen to allow permeation of the electrolytes through the film to a backing cathode. Deposition then starts at the polymer–electrode interface to produce highly wear resistant, reflective and environmentally stable metal deposits which have been grown from the surface into the film. The ascertaining of the roughness of such films is an important criterion of their technological applications. In particular we examine poly-vinylidene fluoride trifluoroethylene copolymer 60–40 films into which a silver layer has been electrodeposited. Ac impedance spectroscopy of the film supported on a stainless steel electrode and in acetonitrile solution is used to characterise the fractal dimension of the polymer-silver interface and the results are correlated with those of optical microscopy. It is found that the former provides a good indication of the surface roughness, whereas this could not be readily predicted from the conditions (deposition potential, charge passed, current density) used to grow the film. Ac impedance data thus provide a non-destructive method for the examination of such hidden surfaces.

2. Experimental

Silver/poly-vinylidene fluoride trifluoroethylene copolymer 60–40 films were prepared by first casting a polymer film on the surface of a stainless steel (type 316) electrode by dropwise addition and evaporation of a polymer solution (10 % wt/vol) in ethyl acetate. The silver film was then grown by the electroreduction of silver nitrate (88.3 mM) from methanol/acetonitrile solution (90 : 10 vol/vol). No additional supporting electrolyte was used. The resulting composite was then rinsed in pure methanol to remove excess silver ions. The charge consumed during electrolysis was obtained by integration of the recorded current/time transient.

Ac impedance measurements were performed using a Solartron 1286 electrochemical interface coupled to a Solartron 1250 frequency analyser. Full ohmic drop compensation was employed throughout. The impedance measurements were made at a stainless steel disc prepared as above. The ac potential applied to the disc (potentiostatted at 0.0 V with respect to the saturated aqueous calomel electrode) was a 10 mV amplitude sine wave, at frequencies of 100 mHz to 65 kHz. All ac impedance measurements were made in the presence of 0.1 M tetrabutylammonium perchlorate in methanol–acetonitrile (90 : 10 vol/vol) solution with no electroactive species present in solution, and at a temperature of 25° C. Before recording data the solution was

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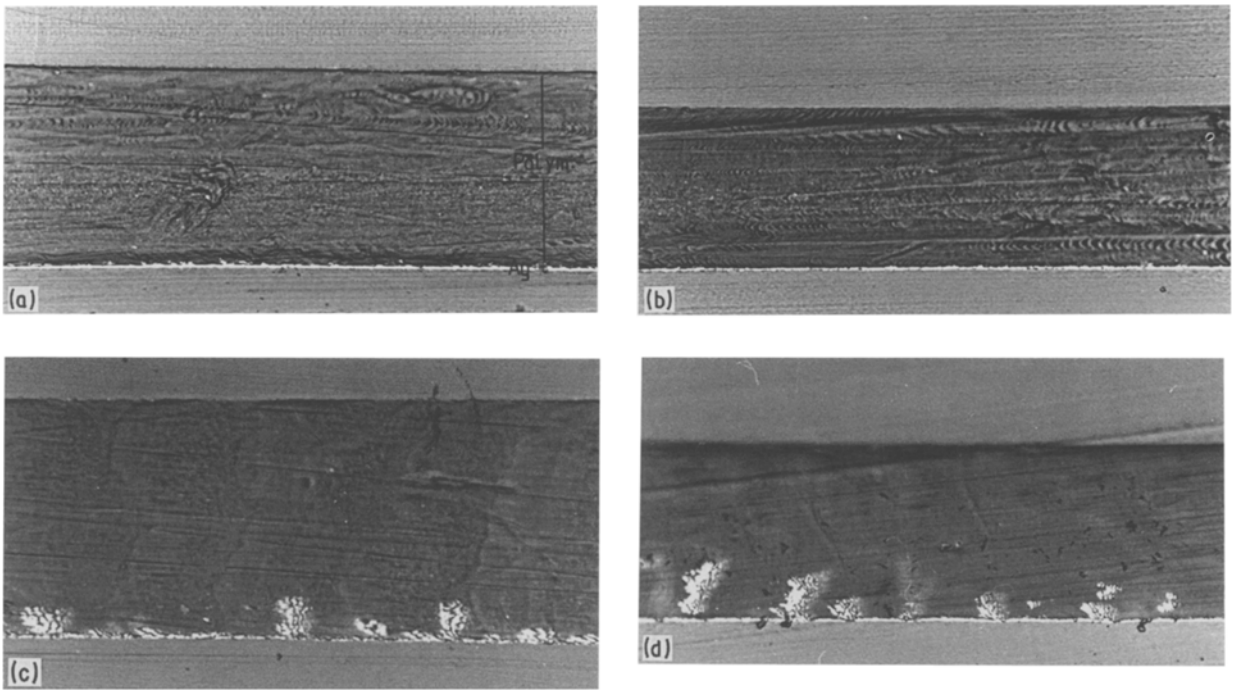

Fig. 1. Optical micrographs of a silver/poly-vinylidene fluoride trifluoroethylene copolymer 60–40 film. Magnification: (a) × 480; (b) × 480; (c) × 720; (d) × 480. Film thickness: (a) 56 μm; (b) 44 μm; (c) 40 μm; (d) 50 μm. The silver layer was grown at a potential (with respect to SCE) of (a) −0.60 V, (b) −0.50 V, (c) −0.60 V, (d) −0.60 V, with the passage of (a) 176 230 mC cm^{-2}, (b) 122 280 mC cm^{-2}, (c) 92 600 mC cm^{-2}, (d) 230 170 mC cm^{-2}. The fractal dimensions deduced from ac impedance measurements were: (a) 2.14; (b) 2.22; (c) 2.35; (d) 2.39.

thoroughly degassed using dried and prepurified BOC (British Oxygen) argon.

Films for optical microscopy were prepared by embedding a thin strip of the plastic film in a cold setting polyester 'SW' type resin before ultra-microtoming (Reichert OMU3). Photographs were taken using a Nikon metallurgical microscope.

3. Results and discussion

Silver/poly-vinylidene fluoride trifluoroethylene copolymer 60–40 films were grown as described above using deposition potentials in the range −0.3 to −0.7 (with respect to SCE). The polymer films had thicknesses ranging from 30 to 56 μm and composites were

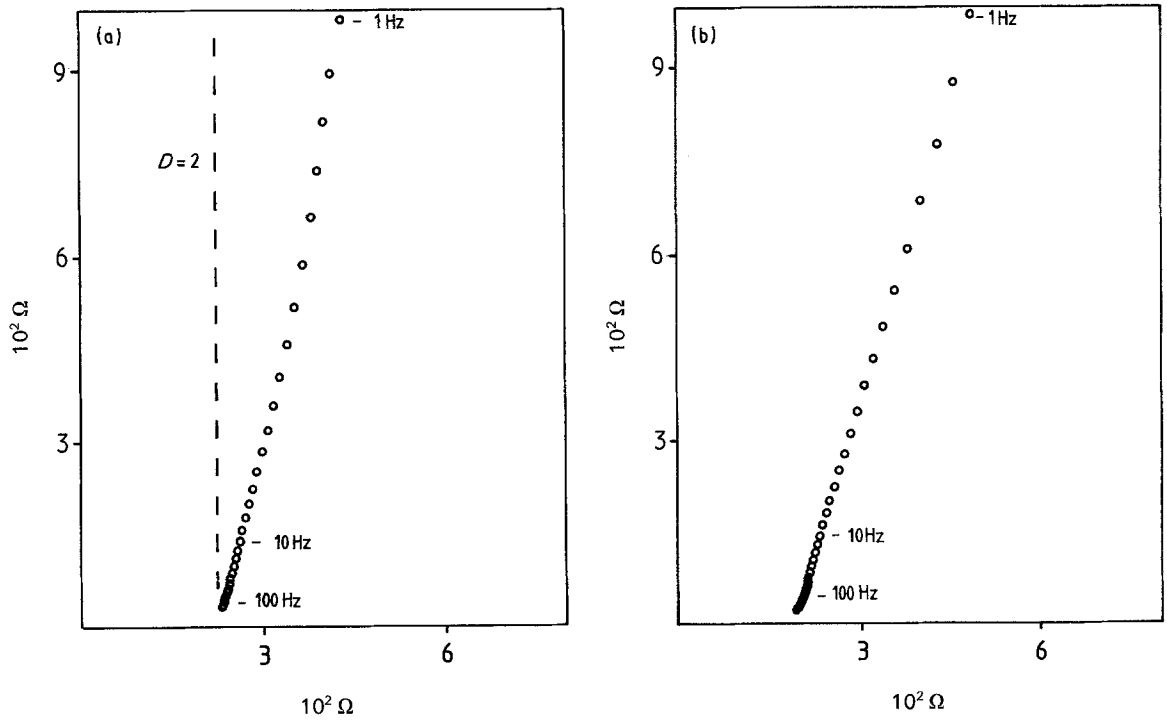

Fig. 2. The complex-plane impedance plots of a stainless steel electrode coated with the polymer/silver film shown in: (a) Fig. 1a; (b) Fig. 1b; (c) Fig. 1c; (d) Fig. 1d — measured at a dc potential of 0.0 V (with respect to SCE).

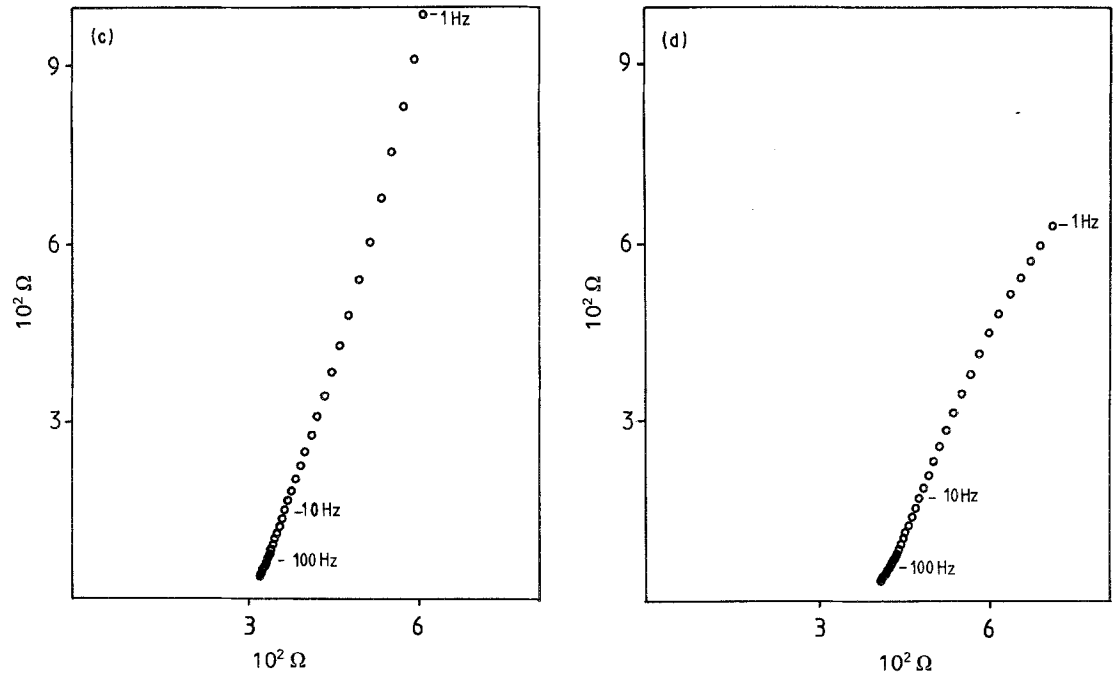

Fig. 2. *Continued.*

grown for a wide range of charge passed in the deposition (46 750 to 834 380 mC cm^{-2}). The films could be readily removed from the stainless electrode and the material produced was examined by optical microscopy. Typical results are shown in Fig. 1a–d. It can be seen that the layer of silver metal formed at the electrode–polymer interface exhibits a highly variable surface geometry that was not readily correlated with the conditions of deposition [11].

Composites, supported on the stainless steel electrode used for their growth, were examined by means of ac impedance measurements conducted with the protocol outlined above. The data corresponding to the four films shown in Fig. 1 are shown in Fig. 2a–d in the form of complex-plane impedance plots, that is, a plot of Z'' against Z' as a function of frequency, where Z'' and Z' are the imaginary and real impedances, respectively. The relationship betwen Z' and Z'' and the total impedance Z is given by

$$Z = Z' - Z''\mathrm{j} \qquad (2)$$

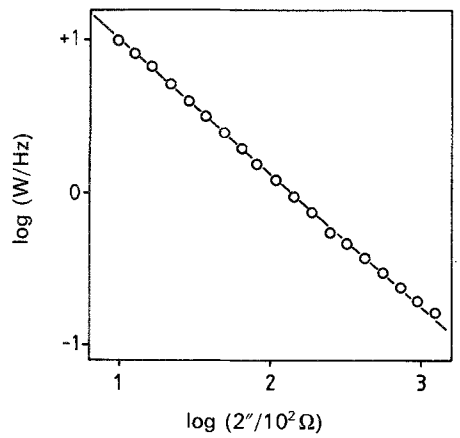

Fig. 3. The analysis of the complex plane impedance data shown in Fig. 2a (see text).

All the figures show a straight line inclined from the vertical axis, as predicted by Equation (1). The angle of inclination permits the deduction of the fractal dimension through analysis exemplified by Fig. 3 in which log Z'' is plotted against log w using the data from Fig. 2a [2–6, 12]. In this way the fractal dimension of the silver surfaces shown in Fig. 1 was deduced as being 2.14, 2.22, 2.35 and 2.39, respectively. It can be seen that these values correlate qualitatively with the roughness observable in Fig. 1.

In conclusion, we have demonstrated that ac experiments can provide a quantitative measurement of the fractal dimension of a metal surface and also provide a suitable non-destructive method for the examination of the surface geometry of metal layers grown within a polymer film.

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