JOURNAL OF APPLIED ELECTROCHEMISTRY **19** (1989) 331–335

Organic/inorganic electrodes (ORINELs) with continuous phase components

B. AURIAN-BLAJENI, S. C. HOLLECK, B. H. JACKMAN

EIC Laboratories, Inc., 111 Downey St., Norwood, MA 02062, USA

Received 11 May 1988; revised 16 August 1988

A new class of composite materials for electrodes is introduced; their characteristic feature is the connectivity of the components. Composites comprising hydrated iridium oxide and polyaniline are characterized by impedance spectroscopy and current pulse experiments.

1. Introduction

For most materials there is a strong relationship between some of their properties and their morphology [1, 2]. One example is iridium oxide, which loses its electrochromic properties when passing from its hydrated amorphous state to its microcrystalline state [3]. One of the drawbacks of this type of material is the sluggishness in responding to electrical perturbations, in particular when movement of ions is involved. In the present work we introduce a new class of electrodes, in which the latter feature is diminished, by reducing the distance traveled by the counter ions. These electrodes are produced by electropolymerization of a monomer in the pores of a disordered matrix, the matrix itself being formed by electrodeposition; we call these electrodes ORINELs (ORganic–INorganic ELectrodes). The difference between this type of composite and related materials is that ideally the two phases present are continuous and interwoven; also the morphology (order, or disorder and general shape) of the matrix is preserved. Related materials would be the organic/inorganic composites in which the matrix is a layered compound and the inserted phase is either an organic molecule [4], or the recently reported polypyrrole formed *in situ* in FeOCl [5]. The process may prove useful for other composite electrodes; for example, this configuration is sought for the composites insertion compound/solid electrolyte [6]. The materials described by us fulfill ideally the theoretical requirements [7].

The main aim of our work was to improve the rate characteristics of the electrodes, and we characterize electrodes thus prepared by impedance spectroscopy and current transient measurements. Some preliminary electron microscopy results are also reported.

2. Experimental details

The substrate for electrodes was an iridium wire 0.5 mm in diameter (m3N from Alfa). Solutions were prepared with water distilled in an all-glass still. Iridium oxide coatings were grown by cycling the electrode potential between −0.25 and 1.25 V vs SCE, at a scan rate of $100\,\mathrm{mV\,s^{-1}}$, in an aqueous solution 0.5 M in H_2SO_4 (Fisher). Aniline (Fisher) was polymerized on the electrode surface by cycling the electrode potential between −0.25 and either 1.0 or 0.8 V vs SCE, at a scan rate of $100\,\mathrm{mV\,s^{-1}}$, in an aqueous solution 0.1 M in aniline and 0.5 M in H_2SO_4. The effects of inhomogeneous current distribution were minimized by masking the tip of the wire with insulating laquer (Miccrostop).

The impedance spectra were measured by means of an M378 system from EG&G, controlled by a PCs Ltd 286^{12} personal computer. Impedance spectra were recorded at various values of the electrode potential, in an aqueous solution 0.5 M in H_2SO_4. The high-frequency perturbation had an amplitude of 5 mV, while the maximum amplitude of the low-frequency perturbation was 10 mV (the low frequency spectra were recorded using the Fourier transform technique).

Cyclic voltammetry measurements were performed using either a potentiostat (ECO Instruments Model 551) driven by a sweep generator (Wavetek model 185) or an EG&G potentiostat (Model 273) that has a built-in sweep generator.

The current pulse experiments were performed with a set-up built at EIC Laboratories, comprising a fast electronic switch/current generator with a 5-ms delay, the waveform generator and two Gates Energy Products batteries (6 V, 5 A) connected in series.

Currents and voltages were recorded either on a Bascom–Turner Instruments data acquisition system (model 8120T), or a Hewlett–Packard plotter.

Our experiments were organized in the following manner: the bare iridium wire was tested and the results compared with the wire coated with iridium oxide, grown to various value of thickness. Then, polyaniline was grown on the oxide-coated wire and measurements were made. We thus minimized the effects of area change due to the manual coating of the wires with Miccrostop.

3. Results and discussion

The formation process of ORINELs is illustrated in Fig. 1. A porous inorganic layer is deposited on a

0021-891X/89 $03.00 + .12

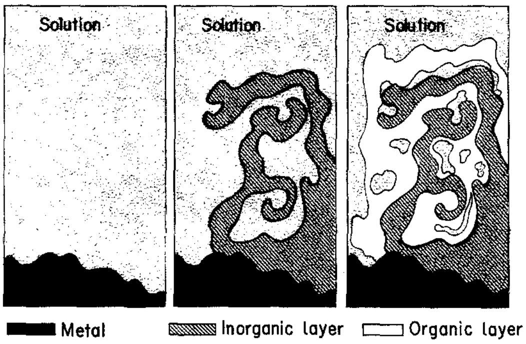

Fig. 1. Scheme depicting ORINEL formation.

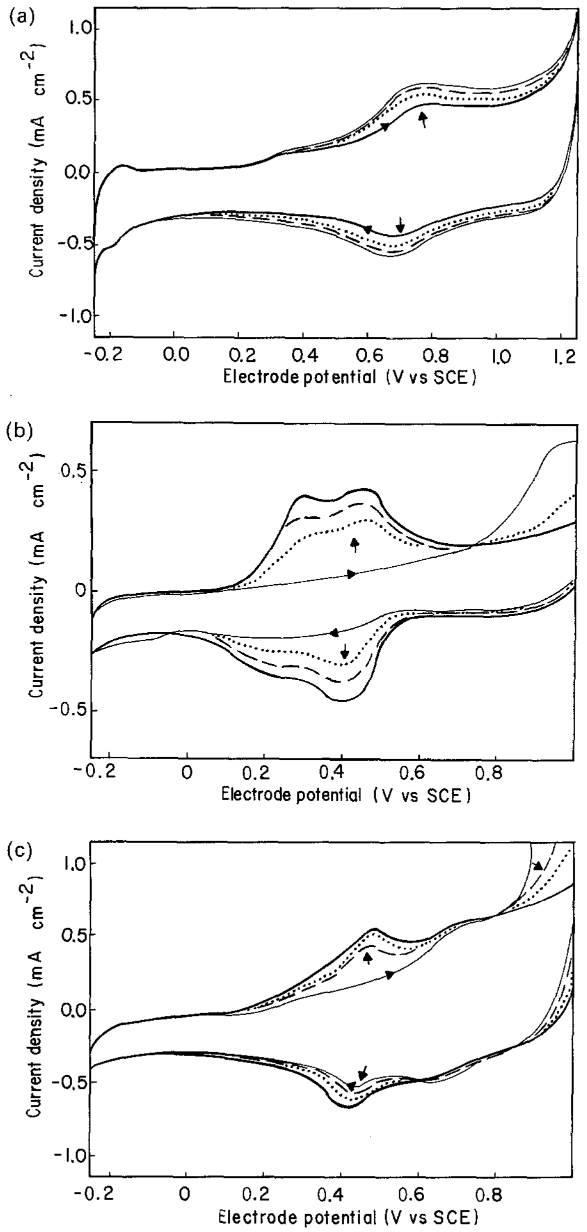

Fig. 2. (a) Growth of iridium oxide layer, by cycling between −0.25 and 1.25 V vs SCE in 0.5 M H_2SO_4. (b) Growth of polyaniline on a bare iridium wire by cycling in 0.1 M H_2SO_4/0.01 M aniline. (c) Growth of polyaniline by cycling the electrode from (a) in 0.1 M H_2SO_4/0.01 M aniline. All the spectra were recorded at 100 mV s^{-1}. The arrows show the time evolution.

metal substrate. The electrode is then immersed in a solution containing the monomer to be polymerized; the polymerization is started after the monomer solution penetrates the porous structure. In the case of a conducting polymer, the polymer film may act as a sink/reservoir for the counterions necessary to balance the redox process occurring in the inorganic oxide film. The same role is played by the inorganic film with respect to the conducting polymer. The counterions are provided by the external electrolyte, of which a part is also trapped in the ORINEL during the polymerization process. This structure preserves the disordered character of the inorganic polymerization matrix, but shortens the distance traveled by counterions. A characteristic feature is that, although the two solid phases in the composite are intimately mixed, they are also connected. By connectedness we mean that between any two points in a solid phase there is a continuous path inside that phase. This is a major difference from the mechanically mixed composites.

An example of the type of composite described is the ORINEL formed in the iridium dioxide/polyaniline system. We took advantage of the fact that iridium oxide does not grow but by cycling between cathodic and anodic potentials in order to make sure that no oxide growth occurs during the electropolymerization of aniline at values of potential inside that window. Figure 2a presents the growth of an iridium oxide film on an iridium wire, characterized by the peak at *ca* 700 mV vs SCE. Figure 2b shows the growth of a polyaniline film on a smooth iridium wire, characterized by large current in the region 0 to 600 mV vs SCE. Figure 2c shows the electropolymerization of aniline at the iridium electrode covered with iridium oxide from Fig. 2a. The polyaniline peak obscures eventually the iridium oxide peak. The three cyclic voltammograms of the film growth show the following: (a) the electropolymerization of aniline on the iridium wire is analogous to the process on smooth platinum showing a three-electron transfer [8]; (b) during the electropolymerization process the redox peak of iridium oxide is evident. These two observations would suggest that the polyaniline formed at the iridium oxide electrode behaves differently from that formed at a smooth iridium electrode. This difference in behavior might be the effect of different chemistry and/or different morphology. The morphology of the iridium oxide film was somewhat different to the 'cracked mud' obtained by pulsing [9]. Our films resembled rather craters; the difference might be due to the fact that we prepared electrodes by cycling, i.e. at a much lower rate [9]. The polyaniline film deposited on iridium oxide had a porous structure, in agreement with data in the literature on polyaniline films deposited by cycling in sulfuric acid [10].

In Fig. 3 we show the cyclic voltammograms in 0.5 M H_2SO_4 for the uncoated and the polyaniline-coated iridium oxide electrode. The height of the peaks characteristic for polyaniline decreases by cycling the electrode to 1.0 V vs SCE, although the films were formed at that potential, in agreement with data in the literature [11]. The charge storage capacity of the electrode before coating, evaluated by integration of the cyclic voltammogram recorded at 10 mV s^{-1}, was

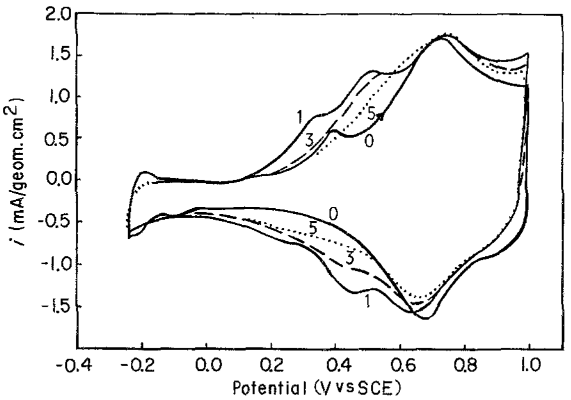

Fig. 3. Cyclic voltammograms of the iridium oxide electrode (0) and the iridium oxide/polyaniline ORINEL in 0.5 M H_2SO_4. The numbers on the curves (1, 3, 5) represent the number of the potential cycle.

42.9 mC cm^{-2}. After coating and 'ageing' by cycling to 1.0 V, the charge storage capacity was 43.4 mC cm^{-2}. Therefore the polyaniline did not affect significantly the charge storage capacity of the electrode within those potential limits. The oxide electrode was stable under cycling. The polyaniline-coated electrode displayed, in the initial sweep, a 25% increase in charge storage capacity over the uncoated electrode. However, after *ca* 5 consecutive potential cycles, the charge storage capacity was similar to the oxide electrode and the peaks specific to polyaniline no longer appeared. The loss of electroactivity did not mean disappearance of the film. In addition to the fact that the peaks characteristic to hydrogen adsorption do not appear, qualitative experiments showed that polyaniline deposited on smooth iridium wire or sheet and cycled to 0.5 V in 0.5 M H_2SO_4 also loses electroactivity but remains on the electrode and even exhibits weak electrochromism (much weaker than the pristine polyaniline). The presence of the polyaniline layer is manifest also in the transient behavior, be it following coulostatic pulses or during a.c. impedance spectroscopic measurements.

In Fig. 4 the results of a coulostatic step experiment on an iridium wire coated with iridium oxide and then with polyaniline are shown. By passing current pulses of 3.22 A geom cm^{-2} for 0.5 ms, the oxide layer is able to supply 1.77 mC geom cm^{-2} with a polarization of 0.56 V, which is still a reasonable value for a 'battery electrode'. The polyaniline-coated electrode can supply only 0.483 mC geom cm^{-2}, undergoing the same amount of polarization. Along the same line, the polarization of a 'fully charged' electrode at this current occurs at a rate of 1025 V s^{-1} in the oxide layer, compared to 3588 V s^{-1} in the ORINEL. The shape of the potential transient of the ORINEL is indicative of the fact that two processes, with different time constants, are superimposed.

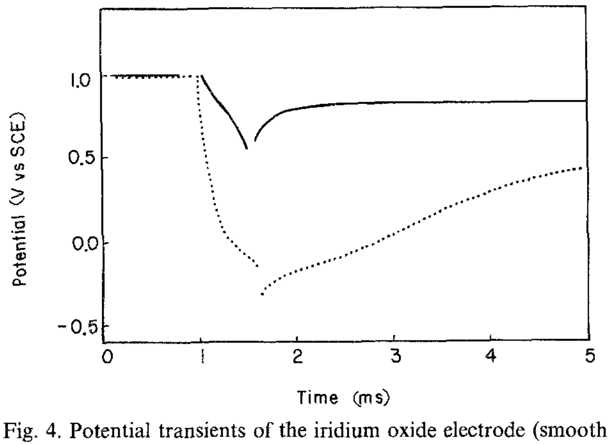

Fig. 4. Potential transients of the iridium oxide electrode (smooth lines) and the iridium oxide/polyaniline ORINEL (dotted lines) upon application of a 3.22 A cm^{-2} pulse for 0.5 ms.

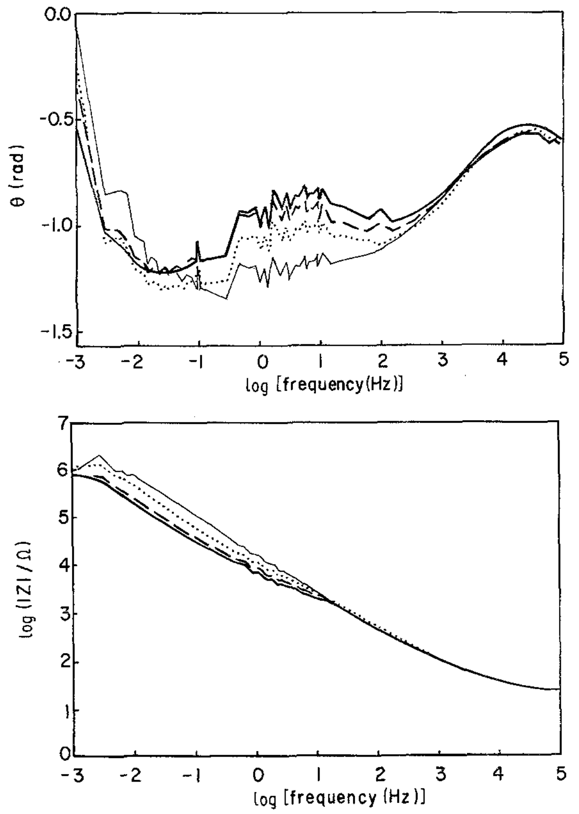

Fig. 5. Impedance spectrum of hydrous iridium oxide, at 0.4 V vs SCE in 0.5 M H_2SO_4 for various values of thickness of the oxide layer: bare iridium wire (thin continuous line); 30 min cycling (dotted line); 60 min cycling (dashed line); 120 min cycling (thick continuous line).

Figure 5 shows the comparison between the impedance spectra of bare iridium and iridium coated with iridium oxide of various thickness expressed as cycling time. It is seen that the spectrum exhibits roughly two relaxation times and the changes due to the growth of iridium oxide are reflected in the low- and medium-frequency regions of the spectrum. The high-frequency region of the spectrum remains virtually unchanged. The modulus of the impedance *decreases* with the growth of the iridium oxide layer. This would be indicative of a surface-limited process; the thicker the iridium oxide layer, the larger the surface and the lower the resistance.

In Fig. 6 is shown the change in the impedance spectrum of an iridium electrode coated with iridium oxide (the thickest from Fig. 5), with the change in the quantity of aniline electropolymerized expressed as time of cycling in solution. It is seen that the effect of thickness appears in the high-frequency range. The effective relaxation frequency is displaced towards

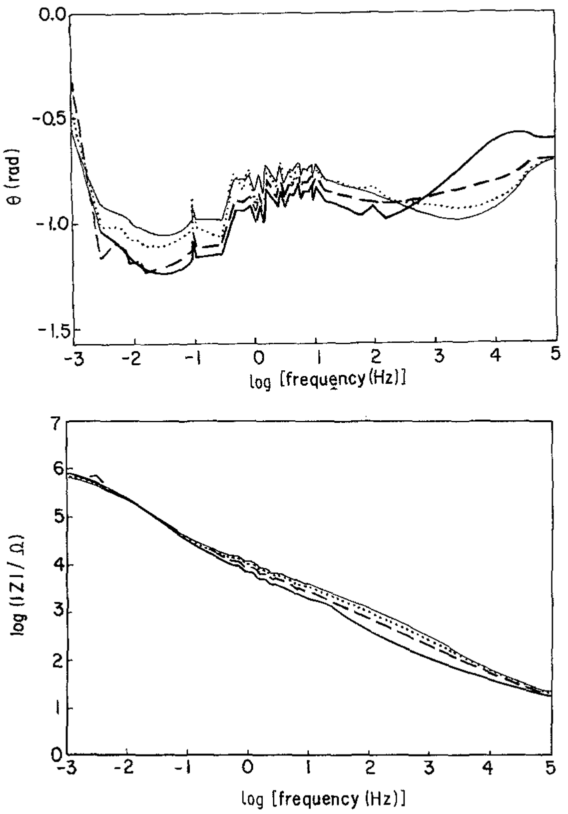

Fig. 6. Impedance spectrum of the hydrous iridium oxide/polyaniline ORINEL at various values of thickness of the polyaniline layer: oxide layer grown by 120 min cycling (thick continuous line); 10 min cycling in aniline solution (dashed line); 33 min cycling in aniline solution (dotted line); 63 min cycling in aniline solution (thin continuous line).

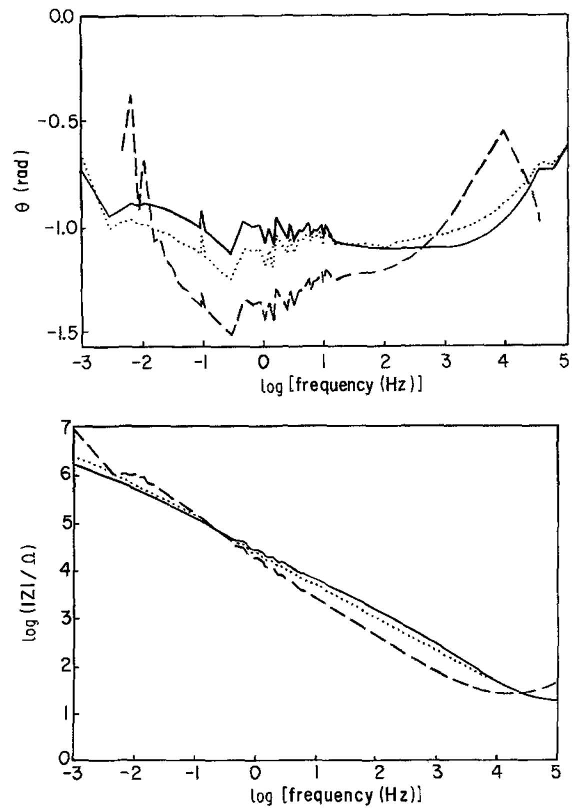

Fig. 7. Impedance spectrum of polyaniline films on iridium wire at two values of the thickness of the polyaniline layer: bare iridium wire (dashed line); 30 min growth (dotted line); 60 min growth (continuous line).

higher frequency, corresponding to shorter relaxation times. The value of the modulus of the impedance in the high-frequency range is higher, in agreement with the current transient results (Fig. 4). The saturation effect with respect to the time of growth in the case of the polyaniline film might be an effect of filling of the accessible pores in the iridium oxide layer. The equivalent circuit of the ORINEL would probably have one more RC element compared with the equivalent circuit proposed by hydrous iridium oxide [12], but the detailed analysis will be presented in a separate study.

Unfortunately, the comparison with a polyaniline film on bare iridium was made difficult by a constant phase element present in the impedance spectrum. This constant phase element (CPE) is prevalent at low frequency. We show in Fig. 7 the spectrum of a polyaniline film on bare iridium. It can be seen that the low- and medium-frequency range is dominated by the CPE (identifiable by the independence of the phase angle of frequency). However the modulus of the impedance is about twice the value in the iridium oxide/polyaniline system, but this might be a result of differences in masking of the iridium wire.

The model of only two elements with characteristic relaxation times is obviously an oversimplification. The complications existing in the system are illustrated in Fig. 1, where we let some solution be incorporated during polymerization. We also show the possible contact between the polymer and the metal of which a great part remains exposed during the growth of oxide [13]. An alternative explanation for the high polarization of the ORINEL during coulostatic pulse could be that the effective surface area accessible at short times is decreased in the ORINEL. However, this is disproved by the displacement of the high-frequency peak in the impedance spectrum towards even higher frequency, suggesting faster relaxation times.

Possible applications of ORINELs would be in electrochromic devices with improved switching performance, in 'supercapacitors' with good rate characteristics, and, in general, in systems in which the rate of response to perturbation is limited by ionic transport.

It is possible to mechanically prepare mixtures in which the components are above the percolation threshold. However, in such systems the connectivity of ORINELs cannot be insured. The mechanical properties of ORINELs might also be different from the regular mixtures in which one material is dispersed in a matrix.

4. Conclusions

We introduce a new type of composite material of potential relevance for electrochemical devices — ORINEL. This type of composite is prepared by electropolymerization inside a porous matrix. We showed that the rate characteristics of the ORINEL are different from those of the inorganic layer.

Acknowledgements

This research has been supported by grants from SDIO, ONR and NIH. We wish to thank Drs R. D. Rauh and G. L. Holleck for many valuable suggestions.

References

[1] J. M. Ziman, 'Models of Disorder', Cambridge University Press, Cambridge (1979).

[2] B. Aurian-Blajeni, L. S. Robblee, A. G. Kimball, G. K. S. Kahanda and M. Tomkiewicz, *J. Electrochem. Soc.* **134** (1987) 2637.

[3] S. Hackwood, A. H. Dayem and G. Beni, *Phys. Rev. B* **26** (1982) 471.

[4] e.g. P. Day, in 'Handbook of Conducting Polymers' (edited by T. A. Skotheim), Marcel Dekker, New York (1986) Vol. 1, p. 117.

[5] M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy and C. R. Kannewurf, *J. Am. Chem. Soc.* **109** (1987) 3797.

[6] e.g. B. Knutz and S. Skaarup, *Solid State Ionics* **18/19** (1986) 783.

[7] S. Atlung, B. Zachau-Christiansen, K. West and T. Jacobsen, *J. Electrochem. Soc.* **131** (1984) 1200.

[8] B. Wang, J. Tang and F. Wang, *Synthetic Metals* **18** (1987) 323.

[9] P. G. Pickup and V. I. Birss, *J. Electrochem. Soc.* **135** (1988) 126.

[10] G. Zotti, S. Cattarin and N. Comisso, *J. Electroanal. Chem.* **239** (1988) 387.

[11] T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.* **17** (1984) 293.

[12] B. Aurian-Blajeni, X. Beebe, R. D. Rauh and T. L. Rose, *Electrochim Acta*, submitted for publication.

[13] B. E. Conway and J. Mozota, *Electrochim. Acta* **28** (1983) 9.