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Electrochemical response of iridium oxide for implanted neural stimulating electrodes

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The electrochemical behaviour of Ir oxide films, grown in neutral PBS saline solution has been examined in relation to their use as neural stimulating electrodes. It is shown that, if adequate growing conditions are chosen, this material is suitable for use as a neural prosthesis, since it is able to pass high values of charge density in a very reversible way, therefore without generating new products to the solution.

1. Introduction

In recent years many implantable electronic devices have been developed, among them neural stimulating electrodes. These are devices intended to interface with the nervous system, using metallic electrodes to stimulate neurones, in an attempt to restore lost neural functions. The most widely used of these implants is the auditory prosthesis where electrical stimulation of the cochlea, by means of a metal electrode placed in the inner ear, causes sound perception for most deaf patients.

In order to achieve electrical stimulation of the nervous system it is necessary to transfer a certain amount of charge density (10 mC/cm^2 [1]) from the electrode through the cells membrane. However, this charge injection process must be reversible, otherwise neural damage can be caused by introducing new species in the tissue that may have harmful effects. Therefore, irreversible Faradaic reactions, such as water electrolysis, gas evolution or metal dissolution must be avoided.

Reversible charge injection is possible either by a capacitive process (double layer charging) or by Faradaic reactions involving species that remain bound to the electrode surface [2]. In this way, it is possible to pass charge through human fluids without generating chemical reaction products.

One of the principal problems related with the neural prosthesis is the lack of selectivity that occurs during neural activation, arising from the large size of the electrodes relative to neurones. For this reason, electrodes designed to be used as stimulating devices are generally very small and thus, one of the requirements for the materials to be employed in these electrodes is the capability to pass very high values of charge density without any detrimental effects [3].

One of the most promising materials for such applications is activated iridium since, compared to any other known materials, it is able to inject the highest charge density for a given applied potential pulse.

The activated iridium consists of a thick multilayered iridium oxide, the thickness of this oxide being directly related to the charge density stored by the material [4]. The iridium oxide film exhibits remarkable electrochemical reversibility and can easily be grown under certain conditions, usually with potential cycling in acid solutions [5].

The high charge injection capacity of this material is the result of reversible changes in the oxidation state of iridium ions in the oxide film. Although the mechanism of this redox process is not completely understood, it is generally accepted that, in order to maintain electroneutrality within the film, either injection of anions from the electrolyte or ejection of cations from the oxide must occur simultaneously with reduction of the iridium atoms [6]. The nature of the ions involved in this process has been the subject of some controversy; some authors favour the involvement of protons [7] whereas others [8] favour hydroxide expulsion during the oxide redox process.

In order to obtain further information on this point, and because the main goal is to generate a material with enhanced electrochemical response to be used as a stimulating electrode, we have studied the film formation and growth in a solution that reproduces the human environment–phosphate buffer saline solution (PBS). In these conditions it is possible to guarantee that the grown multilayered iridium oxide does not incorporate ions other than those present in human fluids, as happens for H_2SO_4-grown Ir oxide that show appreciable incorporation of SO_4^{2-} or HSO_4^- [9].

2. Experimental procedures

The working electrode consisted of 99.9% purity Ir foil (Goodfellow) mounted in epoxy resin. All electrodes were polished to 1 μm DP finish.

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A normal three-compartment glass cell was used, incorporating a Pt wire as counter-electrode and a saturated calomel electrode (SCE) as reference: therefore all potentials are quoted to SCE.

Oxide films were grown in different solutions by repetitive potential cycling between two predefined values, at a constant 100 mV/s sweep rate. Cyclic voltammetry was carried out with an AUTOLAB PGSTAT 20 potentiostat and data were collected by means of appropriate software.

In order to study the influence of the different ions that are incorporated in the PBS electrolyte, different solutions were used to grow the iridium oxide:

- PBS solution (8 g/l NaCl, 1.15 g/l Na_2HPO_4, 0.2 g/l KH_2PO_4 buffered at pH = 6.9)
- 8 g/l NaCl
- 1.15 g/l Na_2HPO_4 + 0.2 g/l KH_2PO_4

Tests were also conducted in 1N H_2SO_4 which is the most widely used solution for growing the oxide, and in order to study the effect of phosphate, solutions with various concentrations of these ions were used: 0.04 M, 0.06 M, 0.1 M and 0.2 M in Na_2HPO_4 and KH_2PO_4 with pH of 6.9.

All solutions used were stirred with a stream of nitrogen gas.

3. Results and discussion

In spite of the fact that it is already well known that 1N H_2SO_4 is a very good electrolyte for growing iridium oxide films via potential cycling [10], (for the reasons already pointed out), we have performed studies on PBS electrolyte (a human-like solution) to see whether it is possible to obtain higher growth rates for the iridium oxide.

For this purpose iridium electrodes were scanned between two fixed potentials, chosen in order to avoid gas evolution, and the external current was measured, after a certain number of potential cycles, and plotted against voltage. Because the sweep rate is constant, the abscissa also represents time, and thus the area under the cyclic voltammogram is a measurement of the total charge transferred which, as has been said before, is associated with the quantity of oxide in the film, i.e. film thickness.

Fig. 1 shows the voltammetric response for pure iridium in PBS (pH = 6.9) and in 1N H_2SO_4 (pH = 1) after 100 potential cycles.

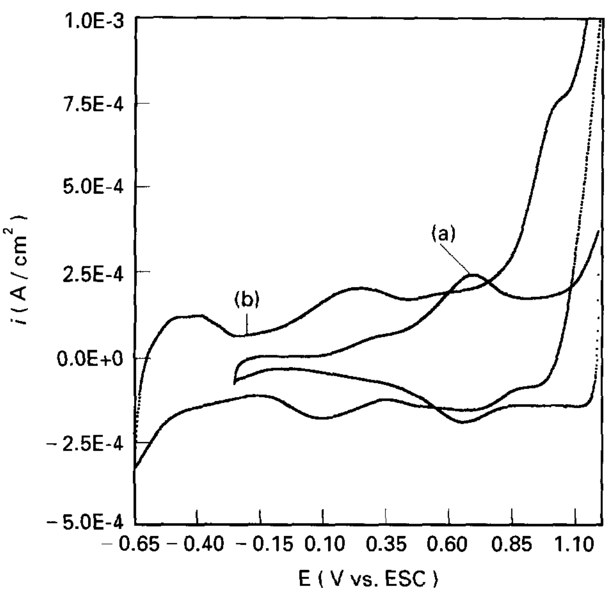

Figure 1 Voltammograms of Ir oxide in (a) 1N H_2SO_4 and (b) the PBS solution (100 mV/s; 100 cycles).

As can be seen, both solutions give similar values of charge density, and the general shape of the voltammogram is similar except for the difference observed in the potentials of the main anodic and cathodic peaks, which are shifted negatively in the case of PBS solution. This difference can be attributed to the difference in pH of the two electrolytes. In fact it agrees with the 80 mV/pH unit decrease observed by other authors [4]. According to McIntyre and co-workers [11], these peaks, which account for the oxide charging and discharging process, are associated with a redox reaction in the anodic film involving a proton–electron dual injection/expulsion mechanism: during positive scan there is proton release from the oxide into the solution accompanied by electron transfer from the metal to the film and the opposite process takes place during the negative scan.

For the saline solution, as a result of the higher value of pH, the reversible potential of this redox reaction is shifted negatively and therefore the main peaks are displayed at lower potentials.

It is therefore possible to inject charge throughout a human-like environment since the redox process that justifies the charging/discharging of iridium oxides is similar and occurs to an equal extent independently of the fact that the oxide film was grown in acid or in the saline media.

However, an intriguing feature appears on the voltammogram performed in the saline solution: a peak is observed at around 1.2 V, visible as a shoulder on the current increase associated with O_2 evolution.

In order to clarify this new feature of the voltammogram and, due to the fact that PBS is a rather complex solution, we have grown iridium oxide film in the different ionic components of the saline electrolyte.

Fig. 2 shows the voltammetric response, after 100 potential cycles for iridium oxide in PBS, NaCl and in phosphate solutions, the concentrations of these last two solutions being equal to the PBS.

As can be seen the charge density of the oxide grown in NaCl is quite small when compared with the other two electrolytes. This fact could be assigned to the formation of soluble chloro-complexes which would promote film dissolution instead of oxide growth. In fact the formation of chloro-complexes has already been reported for ruthenium in dilute solutions of NaCl [12].

Comparing the voltammetric response of the oxide film grown in PBS and in phosphate buffer we see that the shape of the voltammograms is quite similar, except for the fact that lower charge densities (therefore oxide thickness) are obtained in PBS. This fact is most probably related to the inhibiting effect of the Cl^- ions.

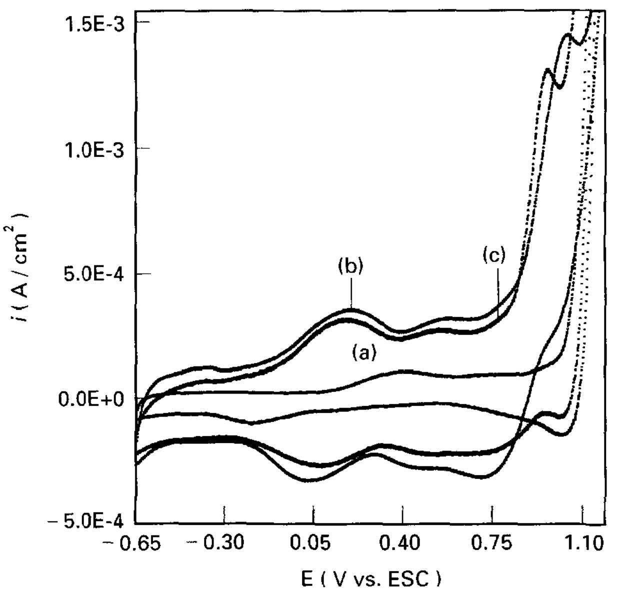

Figure 2 Voltammetric response of Ir oxide after 100 potential cycles in different solutons: (a) 0.8% NaCl; (b) 1.15 g/l Na_2HPO_4 + 0.2 g/l KH_2PO_4; and (c) PBS saline solution.

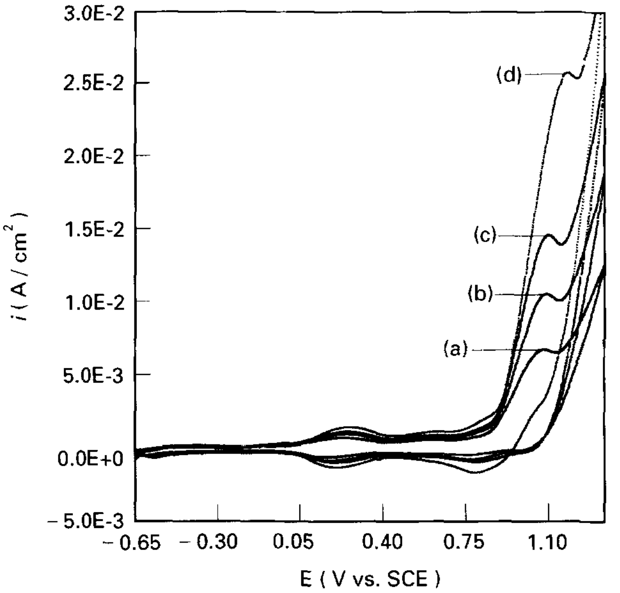

Figure 3 Effect of the different phosphate concentrations on the voltammetric response of iridium oxide: (a) 0.04 M; (b) 0.06 M; (c) 0.1 M; (d) 0.2 M. (100 mV/s; 100 cycles.)

Another aspect that should be noted in these curves is the hysteresis observed between the main anodic and cathodic peaks. This is caused by electrolyte iR effects. To avoid this problem and, in order to clarify the role of phosphate ions, higher concentrations were used to grow the oxide film on this electrode.

Since the shape of the voltammograms does not vary with higher phosphate concentrations it is valid to think that the oxide, grown in more concentrated solutions, is similar to both its thermodynamics and structural aspects, to the one grown in more dilute phosphate solutions.

As can be seen from Fig. 3, where the 100th cycle voltammetric response is shown for the iridium oxide as a function of phosphate concentration, the charge density of the oxide increases with increasing phosphate concentration and the broad peak, just prior to O_2 evolution, is still visible.

TABLE 1 Charge density for the iridium oxide in two different phosphate solutions – influence of the anodic sweep limit

Phosphate buffer concentration	Charge density (mC/cm^2)	
	$E_{\lambda a} = 0.85$ V	$E_{\lambda a} = 1.35$ V
0.04 M	9.88	22.85
0.2 M	19.17	30.11

It is not easy to explain the origin of this peak. However, due to the increase of the current associated with this process with increasing phosphate concentration, it seems logical to ascribe this upper transition to a phosphate ion related process.

Several hypotheses may be considered: (a) oxidation of phosphate ions and, in this case, the peak is not related to the formed oxide. However, according to Pourbaix diagrams, at these potentials there is no evidence of such an oxidation; (b) adsorption of phosphate at the surface; and (c) the development of a higher valence iridium oxide more readily formed by the presence of phosphate ions.

In order to study the influence of this upper potential transition on the growing process, the iridium electrode was cycled to a value ($E_{\lambda a} = 0.85$ V) well below the characteristic potential of this peak, thus excluding the reaction associated with it.

In Table I are shown the results for charge density (and therefore oxide thickness) of the oxide grown in two different phosphate concentrations and for the two different anodic sweep limits.

As can be seen, much higher film thickness was obtained when the upper limit was extended, allowing the process associated with the more anodic peak to occur. This fact seems to indicate that this process should be related to the oxide growth either by an adsorption process or by the formation of a higher valence oxide.

According to Conway and co-workers [4], the growth rate of iridium oxide films is related with adsorption of ions from the solution. In fact, they claimed that this adsorption process is necessary to promote the displacement of metal ions at the metal/oxide interface. However, preliminary XPS studies performed in this laboratory, showed a phosphorous signal for the case of films cycled only up to 0.85 V, which leads us to the conclusion that the observed upper transition should not be related to an adsorption process of phosphate ions. Moreover, Conway and Mozota [4] stated that the incorporation of anions produced by solution dissociation occurs for 1N H_2SO_4, at potentials around 0.4 V vs. SCE, i.e. at the lower anodic peak observed in the voltammogram of Fig. 1.

Due to these findings it seems more plausible to assign this upper peak to a higher valence transition, as is known to happen for ruthenium [13]. This fact should be in some way favoured by the presence of phosphate ions in the solution which promote, by an unknown mechanism, oxide growth.

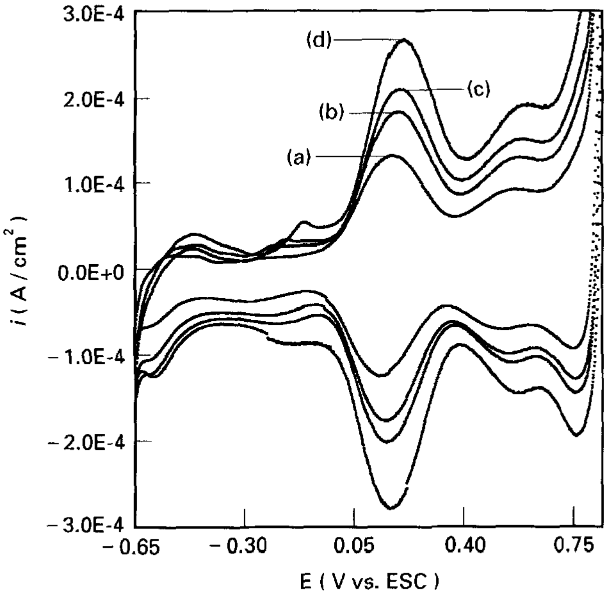

Figure 4 Voltammograms of Ir oxide in different buffer concentrations after 100 applied potential cycles: (a) 0.04 M, (b) 0.06 M; (c) 0.1 M, (d) 0.2 M.

It is noteworthy that a similar voltammetric feature was also reported by Burke and co-workers for thick iridium oxide films grown in alkaline solution [14]. This transition was assigned to the growth of oxide on the electrode, with iridium present in a higher oxidation state (e.g. Ir (V) or Ir (VI)) or to a mixture of both.

Finally, we have studied the effect of different buffer concentrations on the oxide growth rate. Fig. 4 shows the cyclic voltammograms for iridium oxides after 100 cycles. It can be seen that with increasing phosphate buffer concentration, film thickness increases. These results are in disagreement with the findings of Burke [14], who stated that iridium oxide films can be grown in alkaline media only under conditions where the pH of the oxide is made acid enough by the proton release in the anodic sweep. In fact, with higher buffer concentrations those local pH changes would be less effective, but even in those conditions, we obtained higher growth rates.

4. Conclusions

The voltammetric results show that the charge density associated with the charging and discharging process of iridium oxide films is about the same for oxides grown in acid and in a human-like environment (PBS solution).

The results also show that in the human environment the reaction that takes place during oxide charging and discharging processes is reversible.

The above facts assure safe electrical stimulation in this electrolyte since no foreign products are generated in the solution.

The voltammetric curves performed on iridium oxide grown in the PBS solution revealed the presence of a peak just before O_2 evolution. This peak was assigned to the formation of a higher valence state of iridium atoms in the oxide, which enhanced, by an unknown mechanism, oxide growth.

The oxide growth mechanisms that have been proposed so far do not fit entirely our results. The higher oxide growth rates observed with increasing buffer concentrations contradict the statement that oxide growth is not possible in conditions where local pH changes within the film cannot occur.

If the growing conditions are carefully chosen it is possible to obtain charge density values larger than 10 mC/cm^2, which is sufficient to pass through membrane cells in order to provide electrical stimulation of the nervous system.

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