Activated Ir: An Electrode Suitable for Reversible Charge Injection in Saline Solution

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INTRODUCTION

Electrical stimulation of the nervous system with metal electrodes requires reversible charge injection processes to mediate the change in charge carriers at the metal/solution interface and to avoid the formation of toxic electrochemical reaction products (1). Reversible charge injection is possible either by a capacitive process, e.g., double layer charging, or by faradaic reactions involving species that remain bound to the electrode surface.

The multilayer oxide film that is formed on Ir by repetitive potential cycling may produce as much as a 100-fold increase in the charge capacity of the surface (2-4). The increased capacity of so-called "activated" Ir is the result of highly reversible H^+ or OH^- transfer reactions and valence transitions within the oxide layer (4-7). These reactions may provide an ideal mechanism for reversible charge injection providing they proceed reversibly in the in vivo saline environment and occur without excessive dissolution of the oxide. This paper describes the results of our initial evaluation of activated Ir for use as a stimulation electrode.

EXPERIMENTAL

Cyclic voltammetry was carried out with an Amel Model 551 potentiostat programmed with a Bromberg sweep generator, or a Bioanalytical Systems CV-1B voltammetry unit. Potentials were measured against a saturated calomel reference electrode and are reported vs. the reversible hydrogen electrode (RHE).

Iridium electrodes, 0.04 to 0.09 cm^2 geom., consisted of 0.05 cm diameter Ir wire (>99.9% Ir) sealed into Pyrex glass tubing. To obtain an oxide-free, deactivated surface, these electrodes were held for 5 to 10 minutes at 1.9V in 1M H_2SO_4 (3). Iridium microelectrodes, approximately 10^{-6} cm^2 geom., were supplied by M. Bak, National Institute of Neurological and Communicative Disorders and Stroke, NIH. These consisted of 25 μm Ir wire insulated with Parylene-C and having exposed tips of bare Ir 8 to 20 μm in length (8). Electrodes were activated by repetitive potential cycling at 100 mV sec^{-1} between 0.05V and 1.45V in 1M H_2SO_4, as described by others (4). Phosphate-buffered saline (PBS) was also investigated as an alternative electrolyte for activating Ir, particularly for use with the Parylene-insulated microelectrodes. The saline electrolyte contained 0.14M NaCl in 0.1M Na_2HPO_4/NaH_2PO_4 buffer, pH 7.4. In order to standardize our procedures, all electrodes activated for subsequent tests were cycled until the charge capacity in the oxide potential region, 0.4 to 1.4V, approximated 10 $mC \cdot cm^{-2}$.

Biphasic pulse tests and dissolution measurements of activated and deactivated Ir were carried out in 1 ml volume of PBS containing 0.02 wt% human serum albumin (PBS-protein) as described previously for Pt electrodes (9). Because of the low dissolution rates found for Ir, aliquots of pulse solution were analyzed only at the termination of the experiment and not at various time intervals as was done for Pt. Metal analysis was performed by flameless atomic absorption spectrometry. Analytical detection limits for Ir in PBS-protein were determined to be 0.03 to 0.06 μg/ml. Detection limits for Pt in the same solution were 0.01 to 0.02 μg/ml.

The charge limits for water electrolysis were determined with Ir microelectrodes. These were used "as received" or they were activated in PBS as described above. Monophasic, capacitively-coupled stimulation pulses (0.1 ms pulse width, 400 Hz) were applied to microelectrodes in PBS-protein while observing them at 100X magnification for gas bubble formation. The pulse waveform was monitored on an oscilloscope. The stimulation and monitoring circuits are described elsewhere (10). The pulse current

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was increased very slowly until a gas bubble was observed to form at the electrode tip, at which time the current was decreased quickly to about one-half the gassing level. Pulsing was continued for several minutes after which the current was again slowly increased until bubble formation was observed. This procedure was repeated several times to evaluate the reproducibility of the determination. Both anodal and cathodal current pulses were evaluated.

RESULTS AND DISCUSSION

Activation of Ir.—Activation of Ir by repetitive cycling of the potential between 0.05V RHE and 1.45V RHE in PBS produced a progressive increase in charge capacity in the potential region above 0.4V RHE similar to what was observed in 1M H_2SO_4 (Fig. 1). In the saline electrolyte, the main anodic and cathodic current peaks occurred at slightly lower potentials and were less symmetrical about the current axis than in acid solution. However, when an electrode activated in PBS was placed in 1M H_2SO_4 for cyclic voltammetry, the resulting i vs. E curve was typical of Ir that had been activated in H_2SO_4 initially. The shift of peak potentials in the neutral saline is probably an effect due to electrolyte composition and pH (5) rather than due to differences in the oxide film itself. The buffered saline solution, therefore, should be an appropriate electrolyte for activating the type of Ir electrodes designed for in vivo use, such as the microelectrodes evaluated here.

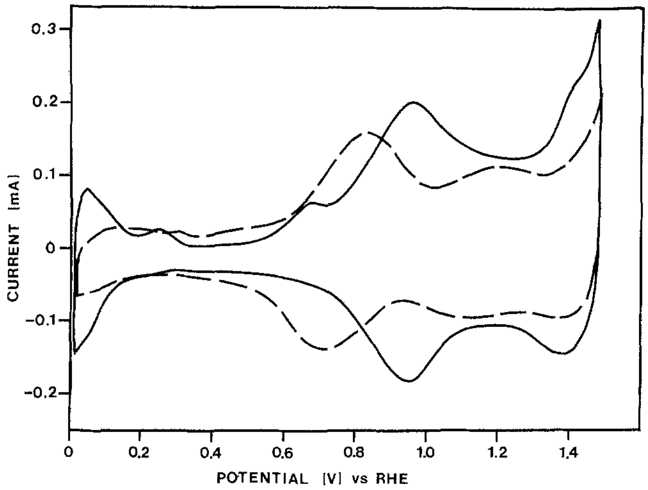

Fig. 1. Cyclic voltammetry curves for Ir after 60 min repetitive potential cycling in 1M H_2SO_4 (solid line) and PBS (dashed line). Scan rate: 100 mV sec^{-1}. Electrode area: 0.09 cm^2 geom. T = 25°C.

Dissolution Tests.—The results of comparative dissolution tests of Ir, Pt and Pt:30% Ir electrodes are shown in Table 1. No dissolution was detected for any of the activated Ir electrodes subjected to anodic-first (AF) biphasic pulses of varying current and charge densities. Deactivated Ir had a significantly greater dissolution than activated Ir with AF pulses of high current and charge density. However, with lower current and charge densities there was no detectable dissolution. Ir dissolution from the Pt:30% Ir alloy was higher than from 100% Ir; Pt dissolution from the alloy was comparable to that from 100% Pt. On the basis of dissolution behavior alone, activated Ir would seem to be the preferred metal for use as a stimulation electrode. The Pt:30% Ir alloy, which is frequently used in stimulation electrodes in place of pure Pt because of its greater mechanical strength, is at a disadvantage due to the likelihood of two metal dissolution products rather than just one.

Gassing Limits.—The evaluation of anodal and cathodal gassing limits for microelectrodes indicated that activation of the Ir surface extended the useful charge injection limits for anodal pulses as much as tenfold (Table 2). There was not as dramatic an effect on charge limits for cathodal pulses, consistent with the charge capacities seen in cyclic voltammograms. For instance, the cathodic charge between 0.7V and 0.0V on a cyclic voltammogram (the possible potential excursion experienced by an electrode during a cathodal pulse) is much less than the anodic charge between 0.7V and 1.45V (the possible potential excursion of an electrode during an anodal pulse).

CONCLUSIONS

Reversible charge injection requires that no new chemical species be produced in solution. With Pt, up to 400 $\mu C \cdot cm^{-2}$ of real area can be injected before the onset of water electrolysis, but a small amount of the injected charge is always lost to metal dissolution (9,11). The results of these initial studies of activated Ir indicate that the charge injection limits for water electrolysis might be increased by a factor of 10 or greater, and that little or no charge is lost to metal dissolution. We conclude that activated Ir is an exceptionally promising material for use as a stimulation electrode. The high capacity for reversible charge injection is of great advantage for applications such as intracortical stimulation of single neurons (12) where the small size of the stimulation electrode, $<10^{-6}$ cm^2 geom., may result in charge densities up to 10 $mC \cdot cm^{-2}$ geom. Moreover, the superior corrosion resistance of activated Ir, compared to Pt or Pt:Ir alloy, will significantly extend the useful lifetime of a chronically implanted neural prosthesis.

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TABLE 1. SUMMARY OF DISSOLUTION STUDIES OF Ir, Pt:30% Ir AND Pt ELECTRODES

Experimental Conditions: Continuous Charge-Balanced Biphasic Pulses; 50 Hz; PBS-Protein Pulse Solution

Electrode Type	Number of Tests	Current Density ($mA \cdot cm^{-2}$)	Charge Density ($\mu C \cdot cm^{-2}$)	Total Time (hr)	Aggregate Charge[1] (coul)	Ir Dissolution (μg)	Pt Dissolution (μg)
Activated Ir (0.04 to 0.09 cm^2 geom)	2	± 800	± 800	66 and 168	931 and 2080	N.D.[2]	
	2	± 400	± 100	48	35	N.D.	
	2	± 200	± 50	48	40	N.D.	
Deactivated Ir (0.04 to 0.09 cm^2 geom)	2	± 800	± 800	48	636	0.16 ± 0.04	
	1	± 800	± 800	24	297	0.46	
	2	± 400	± 100	48	35	N.D.	
	2	± 200	± 50	48	40	N.D.	
Pt:30% Ir (0.09 cm^2 geom)	4	± 800	± 800	48	648	1.85 ± 1.68	2.45 ± 2.24
Pt (0.06 cm^2 geom)	4	± 800	± 800	24	207		1.50 ± 0.16

[1] Charge per phase (anodic or cathodic) x total number of biphasic pulses.

[2] N.D. = None detected. With present analytical detection limits, this may be 0.06 μg or less.

TABLE 2. GASSING LIMITS FOR MICROELECTRODES

Experimental Conditions: Continuous Monophasic Capacitively-Coupled Pulses; 100 μsec Pulse Width; 400 Hz; PBS-Protein Pulse Solution

Electrode Type	Anodic Charge ($mC \cdot cm^{-2}$ geom)	Cathodic Charge ($mC \cdot cm^{-2}$ geom.)
Pt:30% Ir	1.2-1.3	5-5.3
∿3% x 10^{-6} cm^2 geom.	1.3-2.0	0.7-3.3
Ir, As Received	2.0-9.0	1.4
0.8-2 x 10^{-6} cm^2 geom.	1.0-7.0	1.9
Ir, Activated	31-40	3.0-4.0
0.8-1 x 10^{-6} cm^2 geom.	29-30	5.0

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