Electrical Stimulation with Pt Electrodes: II—Estimation of Maximum Surface Redox (Theoretical Non-Gassing) Limits

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Abstract—The maximum, biphasically applied charge which can be injected without electrolyzing water has been determined for Pt electrodes in simulated cerebral spinal fluid at 37°C. Electrolysis of water would lead to gas bubble formation, which is thought to be harmful. The experimental method involved the use of electrical transients. With lead (anodic first) electrodes, the theoretical non-gassing limit is 300 ± 20 μC/real cm^2, independent of current density in the range of ± 50 to ± 450 mA/cm^2. For lag (cathodic first) electrodes, the theoretical non-gassing limit is 350 ± 50 μC/real cm^2 over the same current density range. In both cases, only part of the additional charge beyond these limits results in water electrolysis. Microscopic observations of bubble formation indicate that these limits are conservative. These limits are sufficiently large for most purposes; they do not restrict the use of Pt electrodes in stimulation.

INTRODUCTION

THE purpose of the present series of papers is to determine the safe limits for the use of Pt electrodes for neurological stimulation. In previous papers (1, 2), we indicated that there are three electrochemically safe processes for injecting charge from a noble metal into tissue: These are surface processes. They involve modification of the electrical double layer at the interface or coupling via either of two symmetrical surface-layer oxidation-reduction processes. A key issue to be resolved is how much charge may be injected in a pulse without electrolyzing the electrolyte and evolving gas. We suspect that gas bubbles should be avoided, mostly because they would be expected to be physically disturbing for the tissue. Thus, we should attempt to inject charge via the electrode surface processes described above. If this were so, then the chemical processes at the electrode solution interface would be exactly reversed when the current is reversed during biphasic pulsing. This means that other than minor local, and strictly reversible, pH changes, no electrolytic products would go into solution to cause neurological damage.

It is the purpose of this paper to explore the safe pulse widths we refer to as the "theoretical non-gassing limits" for use of the electrodes. These should not be exceeded, to ensure that we only inject charge via surface processes, and to avoid H_2O electrolysis. Subsequent microchemical analysis is necessary to show whether, even within these non-gassing limits, there are minor reactions, e.g., from Cl$^-$ oxidation and

metal dissolution, which are harmful. These studies will be reported in subsequent publications.

EXPERIMENTAL

Experimental details of the electrodes, the electronic equipment, and the solutions are described in the previous paper (3). As before, experiments were carried out at 37°C using freshly flamed Pt electrodes sealed in glass and biphasically pulsed at 33 Hz. Studies were made in simulated CSF solutions containing added organic matter. Data are expressed in terms of "real area," as measured in $HClO_4$ solution. A method for determining this area in saline and in vivo is described in our previous paper (3).

As before, we distinguish between the "lead" and the "lag" modes of stimulation. In the lead mode, the electrode is first an anode and then a cathode. In the lag mode, the polarities are reversed.

RESULTS AND DISCUSSION

The point where gassing becomes predominant could, in principle, be estimated from the potentials corresponding to the different inflections on these transients (1, 2). It can also be determined from an analysis of the charge relationships between the different processes observed to be occurring during the transient waveforms. Both of these procedures have been investigated.

Potential Transients

Figs. 1-3 show transients for ± 50, ± 150, and ± 450 mA/real cm^2 pulses. The arrows were intended to indicate the points where, based on the observed potentials, we might suppose H_2 evolution from H_2O electrolysis is commencing. Such arrows have been positioned at an inflection point just negative of the reversible hydrogen electrode (RHE) potential. On closer examination, we conclude that this does not correspond to the onset of H_2 evolution. This is for two reasons:

(1) The very negative values of the maximum cathodic potential exclusions during pulsing indicate that H_2 evolution, which normally has little overpotential on Pt (4), is extremely inhibited under these conditions, [*] (e.g., with ± 480 μC/real cm^2 at ± 450 mA/real cm^2, it is -0.70 V). Hence, we cannot infer that H_2-evolution is occurring just from the potentials of the inflections.

[*]This is even after allowance for potential shifts because of local pH excursions (~ 12) during the pulse.
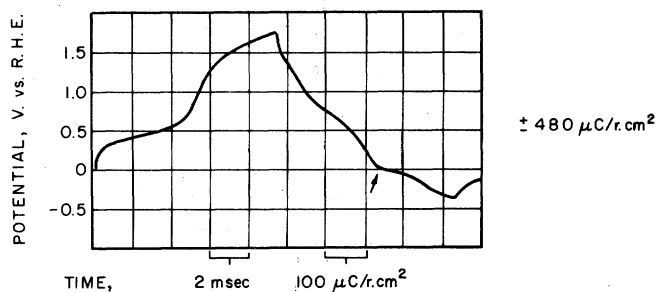
Fig. 1. Potential excursions observed on Pt lead electrode at ±50 mA/r · cm².
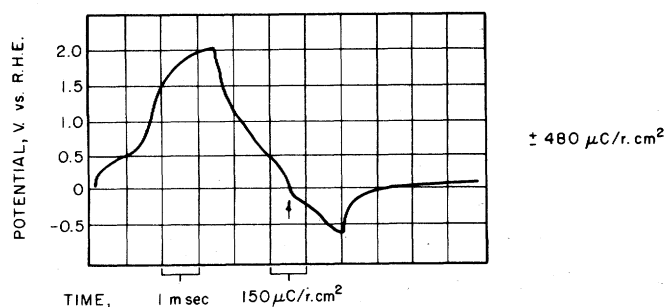
Fig. 2. Potential excursions on a Pt lead electrode at ±150 mA/r · cm².

Fig. 3. Potential excursions observed on Pt lead electrode pulsing with ±480 μC/r · cm² at ±450 mA/r · cm².

Fig. 4. Potential excursion on a Pt lead electrode pulsing with ±1200 μC/r · cm² at ±50 mA/r · cm² (in 3B where the Cl⁻ was substituted by ClO₄⁻).

(2) The voltage-time trace is not flat beyond the inflection, as would be expected for steady H_2 evolution (2).

The difficulty is that the cathodic limbs are not long enough for us to identify H_2 evolution positively. If the charge density during the cathodic pulse is sufficiently increased, there is always eventually a flattening of the cathodal extremity of the potential-time transient when we do reach H_2 evolution. Because of this flattening, we can then tell where H_2 evolution began. Such a complete reduction of the surface, combined with coulometry of the various surface processes, was the focus of our further efforts to determine where water electrolysis begins.

Coulometry of Pulses

For orientation, we refer to Fig. 4. This represents ±1200 μC/real cm² at ±50 mA/real cm² pulses for an inorganic pH 7.31 solution where the Cl⁻ was substituted with ClO₄⁻. The anodic branch of the transient is reminiscent of the classical charging curve for Pt in acid solutions (1, 2). The similarity implies that the main difference of saline from 1M $HClO_4$ results from adsorption of Cl⁻ and not from the difference in pH. The regions marked on the figure are:

HO: Hydride Oxidation (plus double layer)
DL: Double Layer
OF: Oxide Formation (plus double layer)
OE: Oxygen Evolution
O_2R: Oxygen (and oxide) Reduction
OR: Oxide (and oxygen) Reduction
HF: Hydride Formation (plus double layer)
HE: Hydrogen Evolution.

The descriptions of these regions are intended to convey the main processes which they represent. In this particular case,
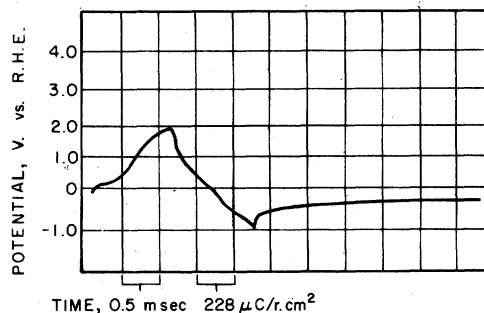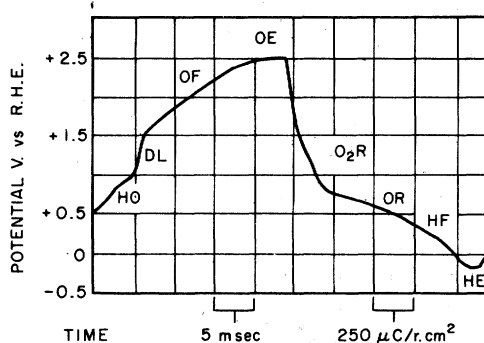
"OR" and "HF" certainly overlap because of the slow kinetics for the reduction of the surface oxide film.

A procedure for estimating the point where water electrolysis begins can be based on the dependence of the charge $Q_{(OR+HF)}$ on Q_a, the anodic pulse charge. The principle is that as long as $Q_{(OR+HF)}$ exceeds Q_a, we will not exhaust the maximum charge which the surface can admit cathodically with a pulse sequence $\pm Q_a$. Hence, we could not reach HE, which always follows completion of HF (4). We should say that any O_2 evolved during Q_a will be partially reduced (up to 50%) (5) during the measurement of $Q_{(OR+HF)}$. If the charge for oxygen evolution, Q_{OE}, were 4% of Q_a, O_2 reduction, Q_{O_2R}, could contribute up to 2% of $Q_{(OR+HF)}$, which is the limit of precision for the measurement. Thus, there must be a 4% uncertainty in knowing the safe limit of Q_a.

The key equivalence to be sought, then, is the point where Q_a just exceeds $Q_{(OR+HF)}$ at each pulsing current density. Correspondingly, we investigated this condition. For this purpose, we interrupted the 33 Hz pulsing sequence at a current reversal point and completely reduced the surface. This involves passing as much cathodic charge as is required to reach H_2 evolution, rather than an amount equal to Q_a.

Representative complete surface reductions after interruptions of lead electrode pulses are shown in Fig. 5(a-c). With the complete reduction current applied, we can clearly pick out the point where H_2 evolution is occurring. We may note that there is frequently a fairly long sloping transient before final flattening. This is undoubtedly due to local pH changes as the pulse progresses. The method of estimating the onset of HE is indicated by the dotted lines in the figures. In all cases, we can pick out the point where HE commences and, especially
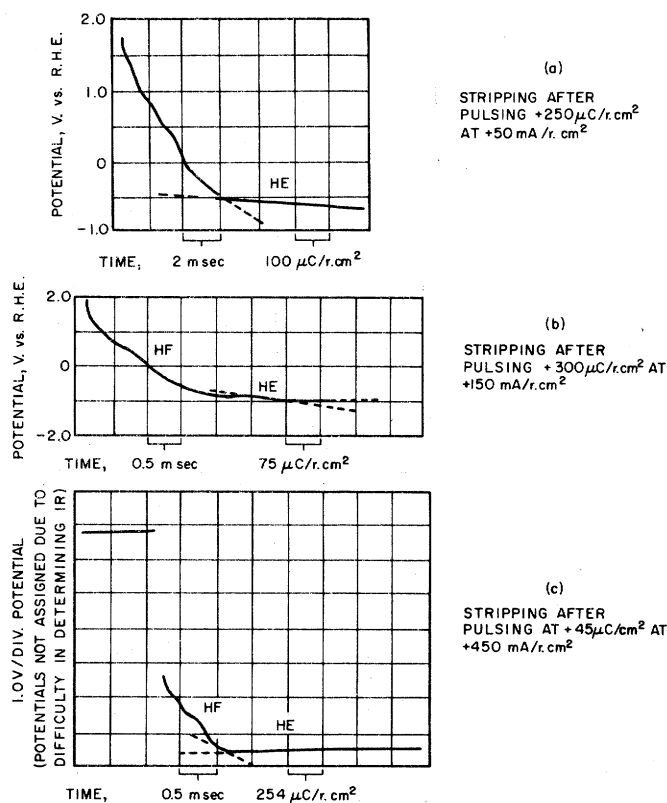
(a)

STRIPPING AFTER
PULSING +250μC/r.cm²
AT +50 mA /r. cm²

(b)

STRIPPING AFTER
PULSING + 300μC/r.cm² AT
+150 mA/r.cm²

(c)

STRIPPING AFTER
PULSING AT + 45μC/cm² AT
+450 mA/r.cm²

Fig. 5. Potential excursions on a Pt lead electrode.

(a)

COMPLETE STRIP WITH
-50 mA/r.cm² AFTER
PULSING WITH ∓160
μC/r.cm² AT ∓50 mA/r.cm²

(b)

COMPLETE STRIP WITH
-150 mA/r. cm² AFTER
PULSING WITH ∓375
μC/r.cm AT ∓150 mA/r.cm²

(c)

COMPLETE STRIP WITH
-217 mA/r.cm² AFTER
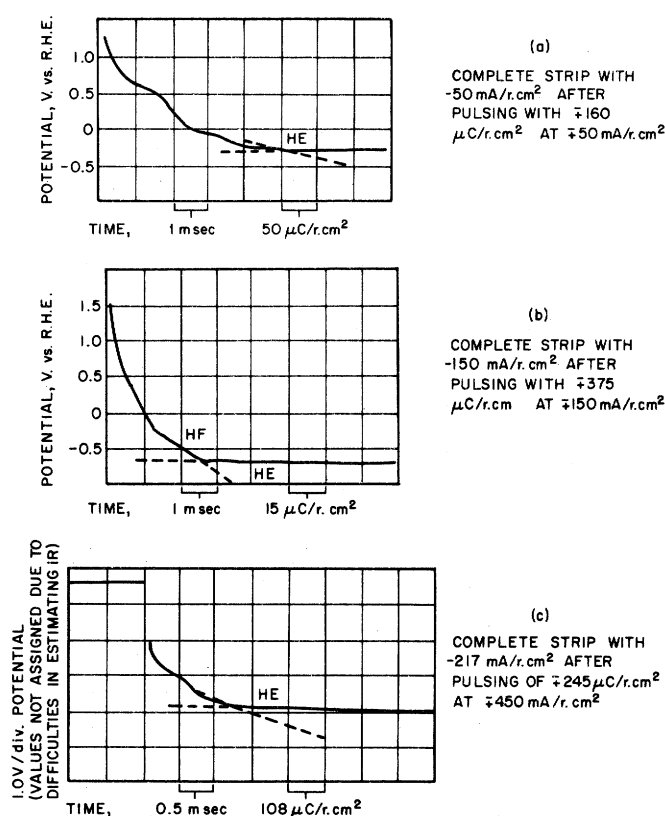PULSING OF ∓245μC/r.cm²
AT ∓450 mA /r. cm²

Fig. 6. Potential excursions on a Pt lag electrode.

for lag electrodes, we can pick out HF quite clearly (Fig. 6(a–c)).

The results from this type of experiment are summarized in Figs. 7 and 8. We see that for lead electrodes the theoretical non-gassing limit is 300 ± 20 μC/real cm² independent of current density. For lag electrodes, the limit is 350 ± 50 μC/real cm² independent of current density.

Exceeding these limits is by no means disastrous, as not all of the excess charge appears to pass into water electrolysis.[**] Under DC conditions, gas evolution is observed under the microscope (100X) at 10 μA/real cm². Under biphasic pulsing conditions ($\pm$ or $\mp$ 50 mA/cm² for lead and lag electrodes, respectively), initiation of bubbling (i.e., not vigorous bubbling) occurs with pulses of $\pm$400 μC/real cm² and $\mp$420 μC/real cm². We estimate from Fig. 7 that under the first of these conditions 20 μC/real cm² of H_2 is evolved. With 33 Hz pulses, this is equivalent to an H_2 evolution rate of 0.66 mA/real cm². Since this greatly exceeds the limits of observability of bubbling by DC currents, the great majority of this H_2 must not have evolved as gas, but must have been oxidized during the anodic pulses of the sequence. We emphasize from this result that the above limits, which we stress are the theoretical limits below which gassing *cannot occur*, are considerably lower than the practical limits.

So far we have only discussed evidence for when H_2 is evolved. Fortunately, we can say on theoretical grounds that if a pulse is wide enough to produce H_2 in solution, it will also be wide enough to produce O_2 on the reverse cycle. The

argument is as follows: If H_2 is evolved cathodically, some of it will escape into solution and not be re-oxidized on the next anodic cycle. This would be true even if the pulsing were continuous, rather than anodic-cathodic-rest, etc. It is clear that with our actual sequence for lag electrodes of anodic-cathodic-long rest, almost all the H_2 which is evolved will actually escape into the solution (dissolved or as bubbles). Since some H_2 is lost from the vicinity of the electrode, the electrode will have to move more positively on the next anodic cycle to find an alternative process to H_2 re-oxidation. If no O_2 is evolved in this more anodic half cycle, less H_2 will be evolved on the next cathodic half cycle.

Eventually, H_2 evolution will cease. If, however, O_2 is evolved anodically, some of it will not be subsequently reduced. We can say then that the absence of other substantial irreversible charge carrying processes, such as saline oxidation or metal dissolution, which we have found is the case, the electrode will shuttle between H_2 and O_2 evolution, if the applied charges are large enough to exceed the maximum capacity of the processes OR + HF. The water electrolysis question then resolves itself to deciding whether *either* H_2 or O_2 is evolved.

Typical stimulation parameters can involve admitting charges of as much as 150 μC/geometric cm² (6). Clearly, then, the present non-gassing limits as such do not restrict the use of Pt electrodes.

REFERENCES

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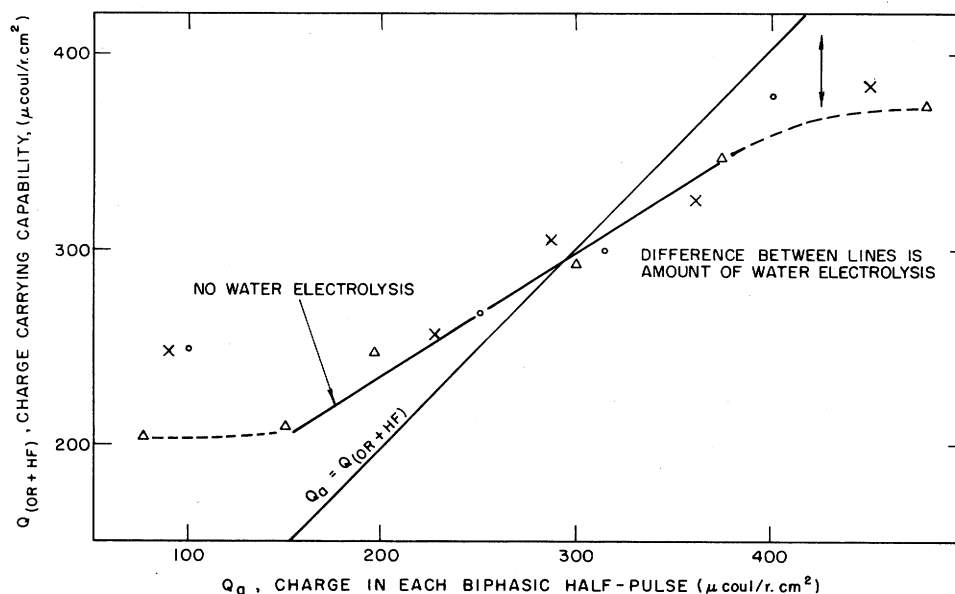
[**]This is because there is more electrode surface oxidation with wider pulses.

Fig. 7. Analysis for nongassing limits on a Pt lead electrode as a function of pulsing current density (o, ±50 mA/r · cm²;
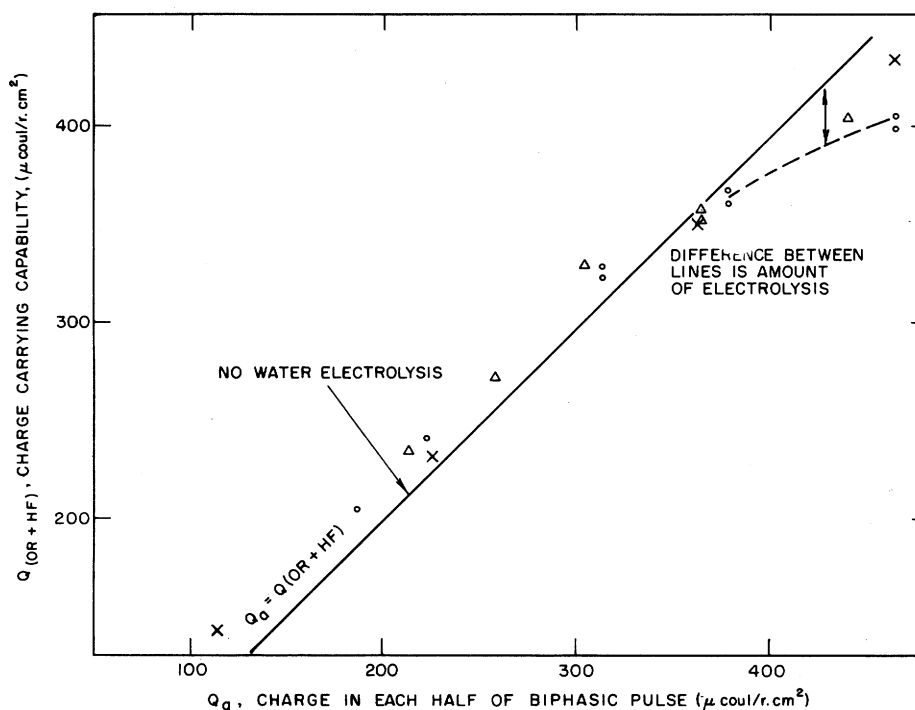Δ, ±150 mA/r · cm²; X, ±450 mA/r · cm²).

Fig. 8. Analysis for nongassing limits on a Pt lag electrode as a function of pulsing current density (o, ∓50 mA/r · cm²;
Δ, ∓150 mA/r · cm²; X, ∓450 mA/r · cm²).

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