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THE SELECTION OF ELECTRODE MATERIALS FOR ELECTRICAL FISHING

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Abstract

In a marine electric fishing system high intensity current pulses must be passed through sea water from metallic electrodes. In general, this enhances the rate of anodic corrosion. The behaviour of several commonly available materials, when used as sea water electrodes, was studied. The influence of the electrodes on continuous and transient current flow was examined. Certain of the materials had protective surface coatings which gave them some resistance to corrosion and influenced their behaviour as electrodes. It was determined that galvanised steel, although subject to a relatively high rate of corrosion, should be an effective, cheap and expendable electrode material, and that stainless steel, which has significant corrosion resistance, should also be a suitable material.

THE SELECTION OF ELECTRODE MATERIALS FOR ELECTRICAL FISHING

Introduction

Electrical fishing in sea water requires the passage of intense current pulses if effective electric field strengths are to be developed throughout significant volumes of water. 1 It seems unlikely at present that these intense currents could be generated purely by induction. Direct current injection is inescapable therefore, and highly conducting materials, i.e. metals, must be used as electrodes. The passage of intense currents from metallic electrodes into a concentrated electrolyte like sea water will give rise to physical and chemical effects, such as corrosion and polarisation at the metal-solution interface which will affect the flow of current. This article describes tests in which several commonly available metals were used to pass continuous and pulsed current through sea water; the object of the exercise being to select a suitable electrode material from those examined.

The passage of current from metallic electrodes into sea water will result in corrosion of the anodes, unless the electrodes are made from the very expensive inert noble metals (platinum, etc.). Electrode materials containing graphite, and lead electrodes containing graphite and with a patent organic coating have been shown to have significant corrosion resistance. Since electrodes mounted on fishing gear are bound to suffer abrasion during towing, the use of costly materials, even as thin coatings, is impractical, and the obvious course is to accept that the electrodes will be corroded away during operation, and use cheaper expendable materials.

Polarisation, which is the limiting of current flow due to chemical activity at the electrodes, may be a problem with some electrode materials. This could be caused by the build up of low conductivity salts or the evolution of gases, but is, however, likely to be limited by continuous scouring of the electrode surface during towing. The passage of current by the electrodes will create electrolytic cells whose voltages will oppose current flow. The voltages of such cells will depend upon the electrode potentials of the metallic ions involved, and might be as high as 2V.

The ideal electrode material for electrical fishing experiments should be mechanically robust, cheap and expendable. It should not be too rapidly corroded nor too strongly polarised, and the properties of the metal-sea water junction should not seriously distort the shape of any current pulse which it passes. The metals chosen for examination were stainless steel, aluminium, titanium, brass, copper and galvanised steel; several of which have some resistance to corrosion by sea water. Stainless steel, aluminium and titanium resist corrosion by having stable oxide films on the surface. Galvanised steel is protected by a layer of zinc, which is corroded in preference to the iron. It was appreciated that these protective films might influence the conduction process, though not necessarily in an adverse way.

Experimental Procedure

Tests were carried out in a rectangular tank (33 x 33 x 40 cm³) in which there was a continuous flow of sea water. Electrodes were made from stainless steel (EN53A), copper, titanium, aluminium, galvanised steel and brass. Each set of electrodes consisted of two plates roughly 30 cm square by 1.5 mm thick, mounted 38 cm apart on a wooden frame. The simple circuit of Figure 1 was used to examine the AC (50 Hz), DC and pulsed DC behaviour of each set of electrodes. Voltage pulses, rectangular in shape and lasting several seconds, were produced by operating the switch.

Correct operation of the apparatus was checked during each test by replacing the electrodes and sea water load by a high wattage 10 resistor. The current density at the electrodes was varied up to $50A/m^2$. The sea water load presented a resistance of approximately 20.

Measurements

In Figure 2 the current density-voltage (J-V) characteristics for the six sets of electrodes are presented. Current density has been normalised in these graphs. On each graph the J-V curves obtained with DC and 50 Hz AC are given. Hysteresis was observed in the DC measurements on titanium and stainless steel, but in the latter case the effect was too slight, and decayed too rapidly to be meaningfully recorded in Figure 2. The DC characteristics are markedly non-linear, and the voltage at which the change in slope occurs is for convenience called the transition point. Aluminium was the only material to have a non-linear AC characteristic.

Under pulsed conditions a marked difference in current flow was noted depending on whether the applied voltage was above or below the transition value. Below transition the shape of the current pulse was the same for all of the electrode materials, and is shown in Figure 3(1). Above transition the shape was different for each material, and the current pulse shapes are recorded in Figure 3(2). These pulse shapes were obtained by the application of a rectangular voltage pulse, and were reproducible in the sense that the shapes, though not necessarily the amplitudes, of the initial transients were always the same.

Corrosion took place strongly at the anodes during the tests, and gns was evolved at the cathodes. Electrolytic cells were created with voltages normally under 1V, rapidly decaying to less than 0.5V when the electrodes were shorted. Observations made when the electrodes were new, and after 30 minutes or more of use, did not reveal any significant differences in either continuous or pulsed operation. With two pieces of galvanised steel wire as electrodes, the current density at the electrode surface was raised to 10⁴ A/m². No current limiting was observed.

Discussion

It is clear from the non-linear nature of many of the DC and pulsed characteristics presented above that the electrode material can significantly influence the passage of current. Since current flow in the sea water is clearly ohmic at the current densities used, processes taking place at the electrode surface must have been responsible for the non-linearities. Several mechanisms are probably involved, but most of the observed effects can be ascribed to the creation of electrolytic cells and the formation of rectifying contacts due to the presence of semi-conducting or insulating salt layers on the electrodes. Polarisation effects in the layer of water next to the electrodes (space charge effects) do not appear to be present as there is no current limiting in the high current region. A brief qualitative consideration of the observed effects follows, attempting to account for some of the observed behaviour in terms of solid state theory.

The DC current-voltage characteristics, excluding those of titanium, could result simply from the formation of electrolytic cells. On the other hand, these characteristics were observed as soon as tests started, before the plates of the cell could have been rendered chemically different by the passage of current and hence polarised with respect to each other. Slight differences in the plates, e.g. non-uniformities in the protective salt layers, may, however, have been sufficient for the creation of a cell immediately on immersion in the electrolyte. The formation of electrolytic cells must clearly have made some contribution to the non-linearity of the DC characteristics, but is unlikely to have been responsible for all of it. The DC characteristics are typical of those produced by rectifying contacts, in which a barrier voltage must be overcome before current can pass.

Two identical electrodes were used in each test, and two barriers must have been present, one forward biased and one reverse biased; only the

latter impeding current flow. The oxide layers present on stainless steel, aluminium and titanium will have energy band structures different to those of their host metals. They may be semiconductors or insulators, and there will therefore be a rectifying junction between metal and oxide. The salts deposited by electrolysis will probably tend to complicate the barrier properties. A very thin layer, several atoms thick, on the electrode surface, could be enough to produce a barrier. Hysteresis was observed with titanium (strongly) and with stainless steel (weakly). This could arise with a metal-semiconductor junction if current flow involved a complex conduction process, such as tunnelling, which required a higher level of energy to initiate it than to maintain it. Pitting was observed on the titanium and stainless steel anodes, suggesting that the surface oxide layer was being broken down in places. This effect probably causes non-uniform current flow close to the anode.

The pulsed observations, below the transition voltage, suggest that the surface layer is similar to a capacitor, with an exponentially decaying charging current. The capacitance must be that of the junction layer, and this appears to be similar in value in every case, except for aluminium. Provided that this capacitance presents negligible series reactance it will not influence the AC characteristic. If, however, it is not negligible, and if in addition the barrier width is voltage dependent (a reasonable assumption) then the capacitance will change with voltage, and the AC characteristic, as in the case of aluminium, will be voltage dependent. The transient conditions with aluminium electrodes will clearly be complex. The differences in transient behaviour above the transition voltage are important, and are likely to be due to differences in the contact barriers and/or in the energy levels of the surface films. Distortion of the leading edge of the current pulse is undecirable, and is most marked in the cases of aluminium and titanium.

Exponentially chaped current pulses are most suitable for use in electric fishing systems. These are generated by capacitor discharge circuits which have high peak and low mean power requirements. In circuits using thyristors the peak of the current pulse can occur within 30 µSec of the start of current flow and consequently can be limited by transient effects at the electrode - sea water boundary. Since the object of passing current through sea water is to influence the behaviour of fish, mainly by induced muscular effects, the minimum contraction time of fish muscle is an important parameter in the design of electrical fishing systems. Muscular contractions can take place in a few milliseconds⁵. Consequently the maximum permissible rise time of the current is about 1 m Sec.

The barrier layers on titanium and aluminium clearly have drastic effects on the transmission of current pulses, making them unsuitable for use as electrodes in experimental conditions where unnecessary distorting factors must be excluded. Severe corrosion took place on the anodes when galvanised steel and copper were tested. It was found, however, that the salts evolved on the anodes of these metals tended not to adhere, and had no limiting effect on current flow. If used as an electrode on a trawl, abrasion during towing would remove these deposited salts even more rapidly. Stainless steel, galvanised steel, copper or brass could be used as electrode materials without undue distortion of current flow. Stainless steel and brass are the most attractive of these metals because of their greater resistance to corrosion by sea water, and stainless steel appears to be the most suitable of these because it is cheaper, mechanically stronger and readily available in useful forms, such as trawl warp. If aquarium experiments are to be conducted, however, the most suitable electrode material would be mild steel, containing no elements which are poiscnous. Copper, nickel and zinc, found in the other likely materials, are considered poisonous. Corrosion of the electrodes will take place

in a marine environment even when there is no impressed current, and anything which limits corrosion will prolong the life of the electrodes. No tests were carried out in which anode and cathode were of different materials, but it is conceivable that the corrosion-resisting properties of titanium could be utilised by having titanium cathodes.

Kreutzer⁶ proposed current reversal as a means of limiting electrode corrosion. The high voltage system which he designed produced oscillatory pulses with inherent current reversal properties. Current reversal prevents the build up of salts during operation but does not necessarily prevent the removal of metallic ions from the electrodes. Corrosion may be inhibited, but the electrodes will still corrode when unenergised. For some applications, e.g. where taxis is to be used, current reversal is not possible. In economic terms the value of current reversal in limiting corrosion would be determined by the relative costs of the electrode material and of the more complex pulse generator.

Conclusion

Stainless steel was selected as the most suitable material for use as an electrode in electrical fishing experiments. Its only drawback appears to be that it contains metals which, if sufficiently concentrated, can be poisonous to fish. If electrical fishing becomes commercially practical the most suitable electrode material would appear to be old galvanised steel warp, which is readily available, very cheap, and expendable.

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FIGURE 1 Circuit Diagram

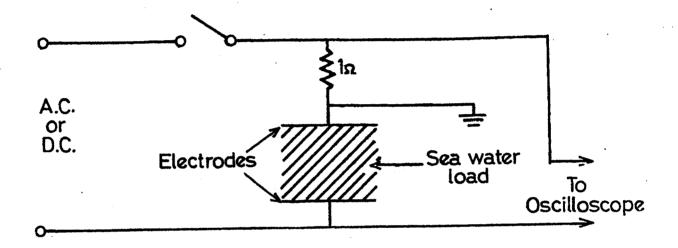
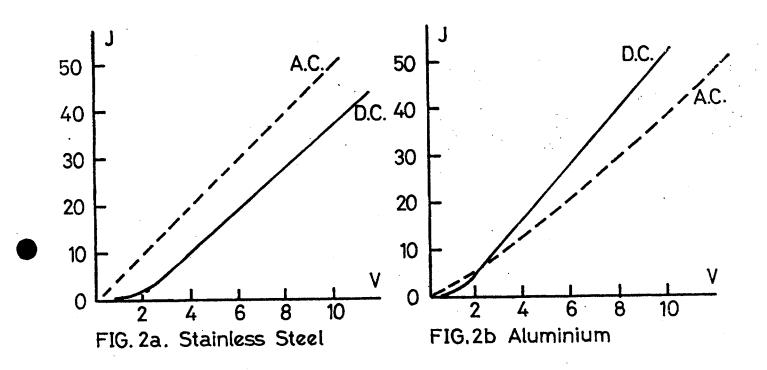


FIGURE 2 Current Density (J) in A/m² plotted against applied voltage (V) for various electrode materials.



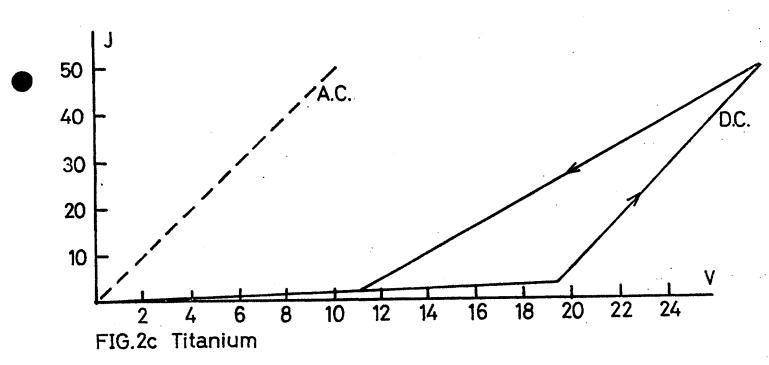
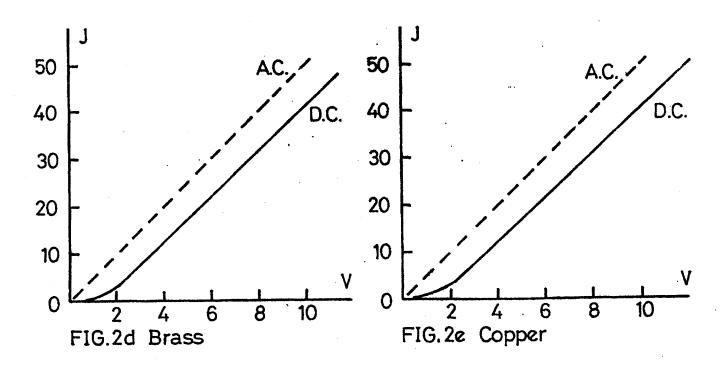


FIGURE 2 (continued)



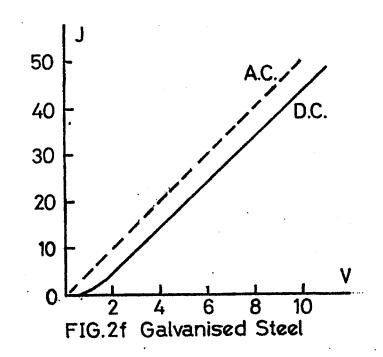


FIGURE 3 Current Pulse Shapes with various Electrode Materials

