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Fabrication of Ag/AgCl electrode for detection of electric field in marine environment

Mohammed Shafeeq KK¹, Shiny Nair², Dr. G. Uma³, Dr. T. Mukundan⁴

¹National Institute of Technology, Tiruchirapalli-620015

²DRDO-Naval Physical and Oceanographic Laboratory, Kochi-21

³National Institute of Technology, Tiruchirapalli-620015

⁴DRDO-Naval Physical and Oceanographic Laboratory, Kochi-21

Abstract: Underwater Electric Potential (UEP) and Extra Low Frequency Electric field (ELFE) measurement is very important and essential for defence and civilian applications. UEP signature is produced by an underwater vessel by corrosion currents in the ship or submarine hull and also from propeller or other dissimilar metallic material in contact with the salt / sea water. The hull of the ship and the propulsion also produces a modulation of the corrosion currents, which is called the ELFE signature. The underwater electric field detection is very important to find the presence or proximity of alien, or enemy underwater targets and their positioning by non-acoustic methods, in the defence sector. The electric field in the marine environment is measured usually with sensor electrodes that are either carbon fibre or silver/silver chloride (Ag/AgCl) based. The typical sensor system uses six electrodes, mounted on three orthogonal axes. By measuring the potential the potential difference between each pair of electrode, the electric field magnitude and the direction of source can be determined.

In this study, Ag/AgCl electrodes have been fabricated by two different methods, thermal and thermal-electrolytic for the purpose of detection of marine electric field. Ag/AgCl electrodes, being reversible electrochemical electrodes, are ideal for measurement of marine electric field. Ag/AgCl electrodes have excellent electrochemical characteristics, such as very high ion exchange reaction current and lack of polarization at a low current density. The fabricated electrodes have been subjected to anodization by two different methods at constant potential and constant current, to increase the concentration of chloride ions for achieving fast equilibrium with chloride ions in sea water. The anodization process at constant potential is found comparatively more suitable in the study as it reduces the electrochemical noise associated with the electrode, the results of which are discussed. The electric field has been simulated in a tank and the characteristics of the fabricated electrodes are studied.

1. Introduction

The detection of electric field signatures such as Underwater Electric Potential (UEP) and Extremely Low Frequency Electric field (ELFE) from underwater vessels, can be employed as a complementary method along with detection using other multi-influence signatures. These methods are important as they find application in defence as well as in civilian arena. In practice, it is inconvenient to try to detect an electric signature by measuring the absolute electrical potential. Instead, the electrical gradient (change in potential) in the water volume near the sensor is measured. A typical sensor thus utilizes two electrodes, mounted 0.2 – 1 meter apart, for each spatial coordinate x, y and z. By measuring the potential difference between each pair of electrodes, the magnitude of electric field and the direction of the source can be found. Most commercial products for UEP/ELFE signal detection are found to have excellent performance specifications, and use either silver silver/chloride (Ag/AgCl) or carbon fibre electrodes, generally arranged on an orthogonal 3-D axis.



2. Fabrication methods

Mainly there are three methods for fabrication of Ag/AgCl electrodes.

- Thermal
- Thermal – Electrolytic
- Electrolytic

The two methods, ‘thermal electrolytic’ and ‘electrolytic’ have been used in this study for the fabrication of electric field sensors.

2.1. Thermal-Electrolytic

Powder metallurgical processes are followed to make the basic green electrode and its surface is further modified by electrochemical methods. The thermal-electrolytic electrode probably has been used more extensively than any other electrode. Typical procedure for fabrication adopted in this study is as follows. Weighed amount of AgCl and Ag were ground, well mixed and sieved in ball mill. The proportion of Ag (fine powder) and AgCl were fixed by trial and error, and that finally arrived was 80:20. After mixing and sieving, the mixture was filled in a mould, specifically designed and fabricated for the electric field electrode.

The mixture of Ag and AgCl was compacted at 2000 Kg/sq.cm with the help of a hydraulic press, the photograph of the mould set up. The green electrode thus obtained was subjected to heat treatment at 100°C for one hour and 450°C for 30 minutes and cooled. Finally the electrode elements were anodized using electrochemical workstation, Autolab PGSTAT 30. The step by step process in thermal- electrolytic method is shown in the flow chart in Fig.1. The Fabricated electrode is shown in Fig.2.

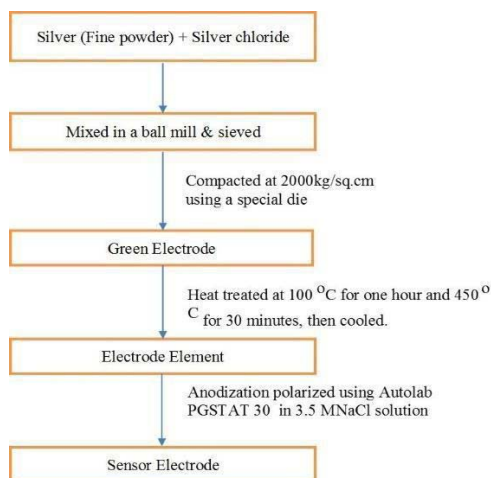


Figure 1. The step by step process for fabrication of electrode by thermal-electrolytic method



Figure 2. The fabricated electrode by thermal – electrolytic method.

3. Anodization process

Anodization, in general is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. Anodization of silver electrode in NaCl or HCl, converts a portion of silver to silver chloride. Anodizing increases resistance to corrosion and wear, and provides better adhesion. With the help of anodization surface unevenness can be reduced and a layer of silver chloride is deposited, that helps in maintaining a constant chloride ion concentration, when the electrode is deployed at sea. This also helps in achieving a fast reversible equilibrium with sea water. The electrochemical noise while measuring the underwater electric potential is also reduced. The anodization can be done by two different methods, constant current and constant potential method.

The electrodes were anodized using an **electrochemical workstation in 3.5 %** solution of sodium chloride at room temperature in a two L beaker inside a dark room. The electrochemical setup used here for anodization was a three electrode setup, as shown in Fig.3. Standard Ag/AgCl was used as the reference electrode and platinum foil used as the counter electrode, for completing the three electrode setup. The fabricated sensor electrode (Ag/AgCl) was connected to WE (working electrode) probe of the workstation and Ag/AgCl reference electrode and platinum foil were connected respectively, to the RE (reference electrode) and CE (counter electrode) probes of PGSTAT 30. Here anodization was done by two methods (constant current and constant potential).



Figure 3. The three electrode electrochemical setup used for anodization and electrochemical noise test

The major challenge during anodizing process was keeping the spacing between three electrodes uniform throughout each and every electrode anodization, to avoid differences related to placement of electrodes. To overcome the challenge, a set up was designed and fabricated comprising of a delrin lid with provision for each of the three electrodes (WE, RE and CE). Six Ag/AgCl electrodes were used for the anodization and further testing. The fabricated electrodes were designated as EF1, EF2, EF3, EF4, EF5 and EF6. Electrodes, EF1, EF2 and EF3 were subjected to anodization by constant potential method and EF4, EF5 and EF6 by constant current. The open circuit potential (OCP) of electrodes anodized by constant potential method was determined prior to anodization. The procedure chosen for OCP measurement with PGSTAT 30 was potentiometry (zero current) in chrono methods (interval time > 0.1 s) for the duration of 3600 seconds. Within the measured period, the potential was observed to achieve a constant value. This value was taken as the OCP of the electrodes. The OCP of all the three electrodes was found to be 0.038 V. For anodization of EF1, EF2 and EF3 at constant potential, a voltage of 50 mV higher than the OCP was applied. The constant potential was applied by the procedure amperometry in chrono methods (interval time > 0.1 s) for a duration of 1000 seconds.

For anodization by constant current, the experiment was performed at constant current of 10 mA. The time for anodization was calculated using faradays first law of electrolysis for a given mass of AgCl deposition. Results are discussed in next chapter. Time for constant current method of anodization was calculated using faraday's law of electrolysis as follows.

$$t = (m \times F) / EI \quad (1)$$

where

t - time

F - Faraday's constant m - mass to be deposited E - Equivalent weight

I - current

4. Electrochemical noise test

It is quite difficult to measure electrochemical noise (ECN) of electrode due to noise of electrode is below micro volt range. Accurate data can be measures only with an electrochemical workstation. In the system need at least three fabricated electrode to measure ECN , and here no need of reference and counter electrode. Here WE, RE and ground probe are connected to three fabricated electrode, S probe is connected with WE probe, and choose the procedure for electrochemical test in Autolab software. In this study ECN test conducted before and after anodization in order to check which anodization is good to reduce electrochemical noise of fabricated electrode.

5. Testing of electrode

The fabricated electrode was tested for the response of electric field in a FRP tank. The measurement set up shown in Fig.4. A high ampere rated DC power supply producing 0-30V was connected to opposite poles with brass electrodes (dipoles) to create electric field in FRP tank. The inter electrode distance and distance between sensor and dipole(brass electrodes) was varied and the values recorded. The inter electrode distance was varied from 30 to 150 cm, keeping the source voltage at 10V and distance between electrode and sensor as constant, that was 2 m.

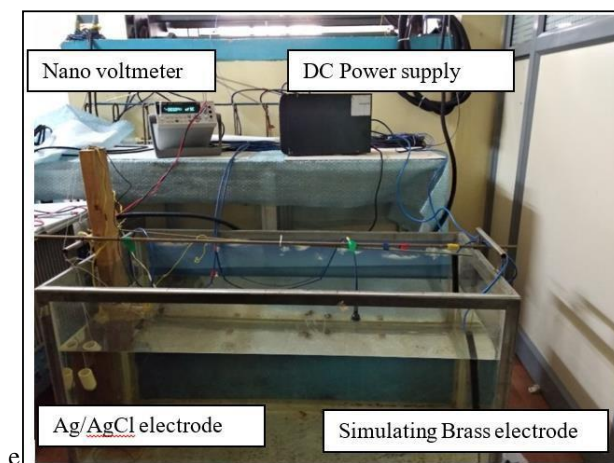


Figure 4. The photograph of testing of electrode setup

6. Results and discussion

The OCP of the Ag/AgCl fabricated by thermo-electrolytic method and anodized by constant potential method were subjected to open circuit potential measurement. The potential vs time graph generated by the Autolab software is given in Fig.5. From the graph the steady values of OCP is found to be 0.038 V. The determined OCP for all the three electrodes, EF1, EF2 and EF3 is more or less similar, which also confirms the uniformity in the fabrication of electrodes by thermo-electrolytic method. A 50 mV of extra voltage was raised and the anodization was conducted for the three electrodes EF1, EF2 and EF3 using constant potential method and the results were analysed from the generated graph shown in Fig.6.

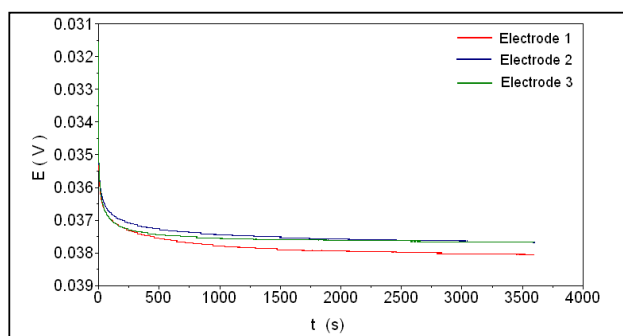


Figure 5. Graph of open circuit potential for electrode EF1, EF2 and EF3

During the process of anodization at constant potential, the exponential decrease in the value of current indicated the increase of thickness of AgCl layer on the electrode surface, thereby the progress in anodization process can also be confirmed. It is also observed that the time versus current curve of each electrode (EF1, EF2 and EF3) is almost identical as compared to the curves for constant current method [Fig. 7].

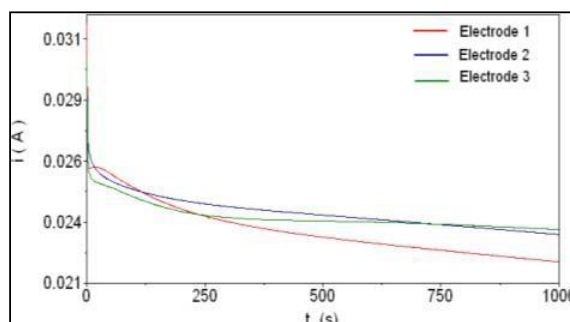


Figure 6. Graph of anodization at constant potential of electrode EF1, EF2 and EF3

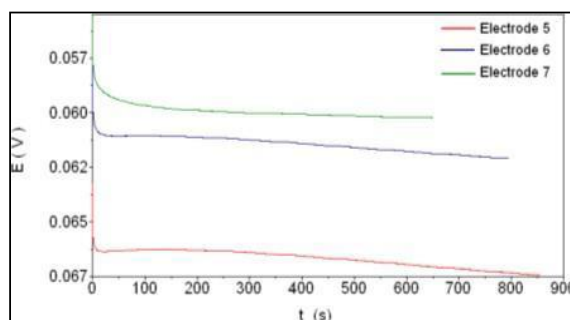


Figure 7. Graph of anodization at constant current of electrode EF4, EF5 and EF6

From the Fig. 7, it is clear that there is a rise in voltage with the progress in anodization at constant current, thereby indicating rise in resistance due to deposition of insulating AgCl. Hence it is concluded that anodization is being carried out. But there is large deviation in the values of potential with respect to time for the three electrodes, EF4, EF5 and EF6. The anodization process is more consistent at constant potential than at constant current. The electrochemical noise of the electrodes subjected to anodization were studied before and after anodization. The observed electrochemical noise after anodization for EF5, EF6 and EF7 is found to be high than EF1, EF2 and EF3 after anodization. Hence, anodization at constant potential is more appropriate for reducing the associated electrochemical noise.

From Fig.8 to Fig.10, the results of electrochemical noise measurement is shown. The electrochemical noise before anodization, as shown in Fig.8, is higher than expected. From the results of electrochemical noise test after anodization, the noise is reduced to a greater extent for electrodes subjected to anodization at constant potential [Fig.9] than at constant current [Fig.10]. Hence, anodization at constant potential is more effective for reducing the electrochemical noise than compared to anodization at constant current.

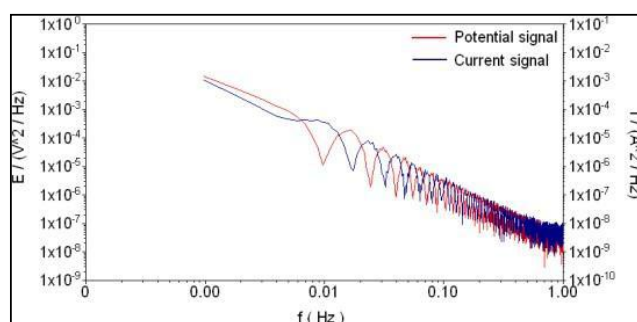


Figure 8. Electrochemical noise before anodization for three fabricated electrode.

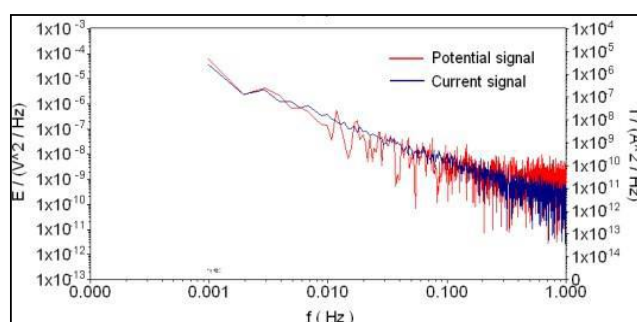


Figure 9. Electrochemical noise for electrodes, EF1, EF2 and EF3.

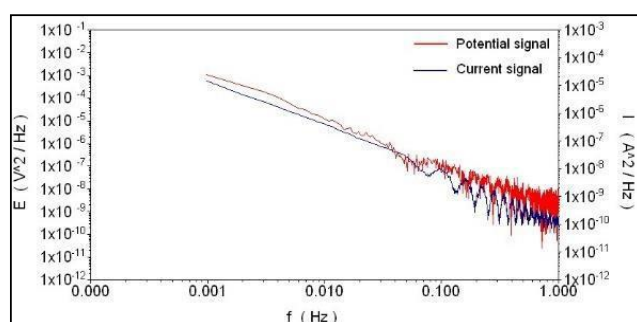


Figure 10. Electrochemical noise for electrodes EF4, EF5 and EF6.

The anodization of the electrodes is responsible for the increased resistance (R) and impedance (Z). The resistance and impedance was measured with impedance analyser to understand the extent of change in R and Z on the electrodes. From the results of measurement of R and Z, it is clear that, evident change in impedance and resistance occur after anodization at constant potential than at constant current.

7. Conclusion

Sensing of electric field generated by vessels in the marine environment is major method of detection by non-acoustic method, which compliments acoustic method of detection. For detection of electric field signatures that are generally of two types, the UEP and ELFE, Ag/AgCl based sensors are used. These sensors are robust, non-polarizable and establish fast electrochemical equilibrium with sea

water. In this study, Ag/AgCl electrodes are fabricated by two methods, thermo-electrolytic and electrolytic. Two dimensions of electrodes, 20 mm and 28 mm were fabricated for studying the effect of surface area. The green electrodes fabricated by electrolytic methods were subjected to electrochemical anodization. An electrochemical set up was realized for the uniform measurement of the electrochemical characteristics, avoiding errors due to placement of electrodes. Among the constant current and constant potential methods of anodization employed, constant potential method was found to reduce the electrochemical noise to a greater extent. A measurement set up involving simulation of electric field using two brass electrodes and field generated by a high ampere rated power supply was employed to measure the response of fabricated Ag/AgCl electrodes by thermal electrolytic method. The electrodes were shown to have linear response with increase in distance between the simulation electrodes and Ag/AgCl electrodes. Fig.11 Shows that testing result of electrode for change in inter electrode distance and change in distance between dipole (DBD).and from the graph (Fig11) it is clear that with increasing the inter-electrode distance sensor voltage increased and also response of electrode is quite linear. Therefore, the electrode is good for measurement of marine electric field. These fabricated electrodes will be compared with the properties of electrodes fabricated by electrolytic method.

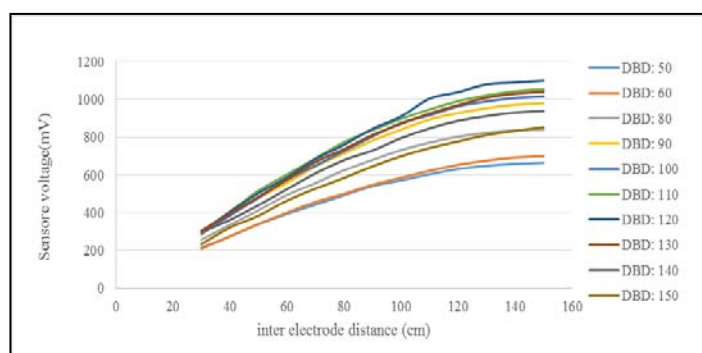


Figure 11. The testing result with different distance between the dipole electrodes

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