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Choice of Electrode Material for Detecting Low Frequency Electric Field in Sea Water

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Abstract. Seven types of electrodes have been selected. DC resistances, AC impedances and voltage difference of the electrode pairs have been studied, according to the requirement of low and extra low frequencies electric fields detection in sea water. The feasibilities of these electrodes used for detecting these signals have been studied and explained on theories. The results show that the all-solid-state Ag/AgCl electrode is the most sensitive electrode with its very low DC resistances, AC impedances and the voltage difference controlled within 20μV, which makes it detecting low frequency electric field accurately.

Introduction

Electrochemistry electrode is usually used for electric field detection in marine environment. The voltage difference between two electrodes was measured to analyze the target electric field in ocean. The material and structure of electrode can affect the stability of electrode voltage in seawater and characteristics of polarization produced by the disturbance of target electric signal, and electrochemical properties of electrode can affect the precision of detecting results. The researches of the electric field detection electrode material are not systematically mentioned in domestic and overseas literature [1], so it should be studied.

Marine low-frequency and extremely low frequency electric field, whose field strength are weak, are produced by superposition of direct electric fields, alternating electric field and syntonic electric field [2].As disturbed by these electric fields, the DC resistance and AC impedance of electrodes change. Some researches show that [3], less resistance and impedance of electrode without disturbance can improve the measurement accuracy of detecting electrodes. In addition, different potential of electrodes is an important characteristic parameter of electrode, and little voltage difference can improve the accuracy of weak signal detection. Therefore, DC resistance, AC impedance and voltage difference of varied electrode pairs are studied to choose the best electrode pair for electrode field detecting. The relationship between the electrochemistry performance and electric field detection is researched to provide the principle of electrode material selection.

Electrode Materials and Experiment Methods

Electrode Materials. Argent electrodes, zinc electrodes, graphite electrodes, carbon fibre electrodes, saturated calomel electrodes (SCE), all-solid-state Ag/AgCl electrodes and the Ag/AgCl electrodes bought from market were selected. Tow types of Ag/AgCl electrode was selected to analyze the performances of electrodes with different structure.

Test Methods. (1) The DC resistance of electrodes: DC resistance was mianly used to study the performance of electrode polarized by direct current signal. The polarization curve could represent response state of electrode pair, and symmetry of the curve decided the ability of electrode to maintain balance of direct current Polarization and stability of signal response.

The traditional three-electrode testing system was used. According to the demand of marine low-frequency electric field detection, working electrodes and reference electrodes of testing system were the same electrode, and the auxiliary electrode was platinum electrode. The electrodes were tested by CS350 electrochemical testing system in 3.5% NaCl solution, and voltage range of DC was

-20~+20mv (relative to open circuit potential). The current density of the electrode surface was recorded automatically by the software of testing system, and then, the E-I curves were made.

(2) The AC impedance of electrodes: It was mianly used to study the response of electrode with the disturbance of alternating current signal. The traditional three-electrode testing system was applied. The working electrodes and reference electrodes of testing system were the same electrode, and the auxiliary electrode was platinum electrode. The electrodes was tested by CS350 electrochemical testing system in 3.5% NaCl solution, and the frequency range of sine wave excitation signal was 0.01Hz -100KHz, and the voltage of alternating current signal was 5mv.

(3) The voltage difference of electrodes: It was mianly used to study the stability of electrode pair. The surfaces of studied electrodes (excepted SCE) were ground to 800# and cleaned by distilled water. The electrode pairs were immersed in 3.5% NaCl solution to be stabilized for 10 min, and then measured the voltage difference with low-noise voltage testing system.

Results and Discussion

The DC Resistance of Electrodes. It can be observed from the E-I curves of electrodes showed in Figure 1 that polarization properties of electrodes composed with varied material are significant difference. The anodic and cathodic polarization curves of Ag/AgCl electrode and saturated calomel electrode are symmetrical, indicating that these electrodes have the best performance to maintain electrochemical balance. That is an inherent feature of the reference electrode. The anodic and cathodic polarization curves of Ag electrode, Zn electrode, graphite electrode and carbon fiber electrode are difficultly symmetrized. The reason is that,in the seawater, cathodic process, normally, is reducting reaction of oxygen on the electrode surfaces, which is greatly different from anodic polarization. Thus, the electrodes can barely maintain electrochemical balance in the short term. Analyzing the anodic and cathodic impedance data of polarization curves listed in Table 1, the resistance of the Ag/AgCl electrode bought from market is up to $6200\Omega\cdot cm^2$, while it of the all-solid-state Ag/AgCl electrode is $320\Omega\cdot cm^2$. The forth one is as almost 20 times as the last one. It is because of that the Ag/AgCl electrodes bought from market are with pyrex glass and porcelain diaphragms, which is used to store internal reference solution, and can make the resistance increase [4]. In addition, saturated calomel electrode with the same structure also have large resistance. Therefore, it can be concluded that ceramic diaphragm structure is not conducive to the performance of electric field detecting electrode. Polarization resistances of graphite electrode and carbon fiber electrode are large,and these electrodes are inert electrodes in seawater, which are different to maintain balance. In addition, the surface area of graphite electrode is wide and rough, which leads to instable polarization curves, and result in significant differences of cathodic and anodic polarization curves. Thus, graphite electrode should not be chose for detecting electrode. The reversibility of carbon fiber electrode is relatively good, and according to correlative report, it is used to be detecting electrode in Sweden. The resistance of Zn electrode is small, but the anodic and cathodic polarization curves of it are extremely difficult to symmetrize, so it is not appropriate as detection electrode.

The result of DC polarization test shows that: the all-solid-state Ag/AgCl electrode have great symmetry of anodic and cathodic polarization curves, good capacity of maintaining balance and reversible state, small resistance, and perfect sensibility. So the all-solid-state Ag/AgCl electrode is suitable as electric field detection electrode in marine environment.

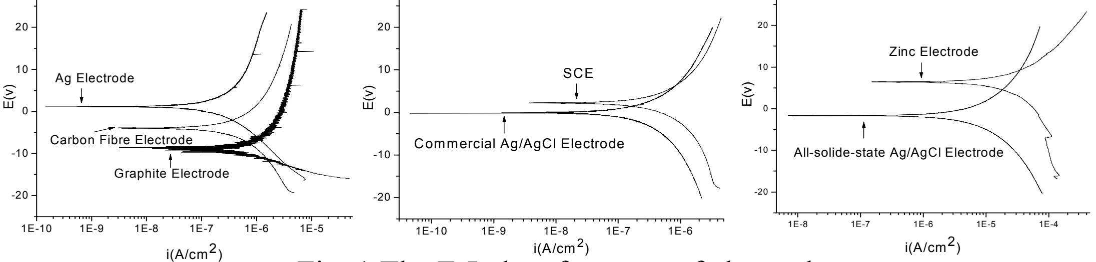

Fig. 1 The E-I plots for types of electrodes

Table 1 Values of resistance for types of electrodes($\Omega\cdot cm^2$)

	SCE	Ag	Zn	Graphite	Carbon fibre	Commercial Ag/AgCl	All-solid-state Ag/AgCl
Anode	4395.8	16236	42.20	5497.6	5853.7	6142.4	363.14
Cathode	5430.4	2284.8	177.8	189.87	3925.6	9135.6	298.15

The AC Impedance of Electrodes. As showed in Figure 2, electrochemical impedance spectrums (EIS) of these seven electrodes unfold diverse trend. The EIS of graphite electrode showed characteristic character controlled by ions diffuse process, and the reason was that the establishment of electrochemistry balance was depended on surface sorption produced by electrolyte ions in solution. The detection principle was that the electric field of vessel could induce the movement of electrolyte ions, which changed the state of electrical double layer and the voltage of electrodes [5]. The change of voltage was tested to characterise the intensity of electric field. So if the voltage of graphite electrode was steady without disturbance of electric field, it can be used for electric field detection in theory. Comparing to graphite electrode, the EIS of carbon fibre electrode was not controlled totally by ions diffuse process. There was a capacitive reactance arc in the low frequency part of the EIS, and the resistance is large which showed that there were active electrochemistry progress on the surface. On the one hand, the length of the carbon fibre was different, the surface area of electrode was large, and the surface state was unstable. On the other hand, the fibre structure can prevent the diffuse movement of electrolyte ions, so the only part controlled by ion diffuse process was the mid-frequency part of EIS curve.

Zinc electrode is solid state electrode and its resistance is small. However, the EIS was the typical figure with double capacitive reactance arc, showing that there was a certain film on the surface. That film may be colloid film produced by aggradation of Zn^{2+} around the electrode. Although the obstructive action of film is not obvious, it could attenuate or change target signal. So zinc electrode is not suitable for electric field detection. The voltage of saturated calomel electrode (SCE) is steady, but it contained ceramic diaphragms and internal reference solution. Electrochemistry process of it was mainly controlled by diffusion,and the impedance value is high. Thus,it was not good for electric field detection. The Ag/AgCl electrode bought from market had similar structure with SCE and represented diffusion character. The capacitive reactance arc of its EIS curve was regular, and the value of resistance is up to $10^3\Omega$. So, it could not be used as probe electrode.

The impedance of all-solid-state Ag/AgCl was rather small, and, in theory, was ideal nonpolarization electrode [6]. As electric charge flowing from out-circuit to interface could be totally taken part in electrochemical reaction, the high speed rate was permitted without damaging the structure of electrical double layer. Even if there was electric current though the circuit, the electrochemical reaction could still grow with balance situation. Thus, the electrode was suitable to detect electric field. The EIS curve of Argent electrode contained a capacitive reactance arc, and the resistance of the electrode was as ten times as that of the all-solid-state Ag/AgCl electrode. So electrochemistry balance of Argent electrode was hard to establish, and the stability was not so well.

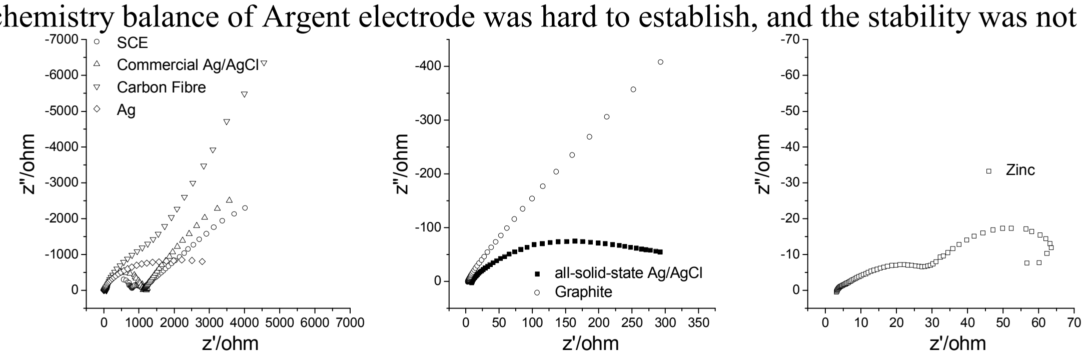

Fig. 2 Nyquist curves for types of electrodes

The Voltage Difference of Electrode Pairs. The voltage difference of electrode pairs is an important characteristic parameter of sensitivity, which can indicate the feasibility of electrode for marine electric field detection. Therefore the voltage difference of nine electrode pairs were tested.

Figure 3 shows voltage difference-time curve of the electrode pairs studied in 3.5% NaCl solution. It can be seen from the figure that the voltage difference of all-solid-state Ag/AgCl electrode, the Ag/AgCl electrode bought from market and carbon fibre electrode pairs are smaller than the others, and the values of them are respectively inside of 20μV, 130μV, 260μV. It can be explained by electric conductive mechanism of electrode: First of all, zinc electrode is difficult to purify with ordinary conditions, so it is mixture. The voltage of the main component and the impurities are difference, and they form a loop with seawater, which reduce the stability of electrode voltage. That is micro cell effect [7]. The voltage difference of all-solid-state Ag/AgCl electrode is the smallest one. The main reason is that silver easily purify, which prevent the micro cell effect [8], and there are many tiny aperture on the electrode surface, which are propitious to the stability of electrode. Secondly, as Ag/AgCl electrode have single electric conductive ion, which is Cl^-, the self-noise of the electrode is further reduced. But the surface electrochemical reaction of other electrodes need OH^-(or H^+) of water, which increase the electrochemical noise of electrode, and decrease the stability. Consequently, as low-frequency electric field signal in the ocean is weak, the electric field detection electrode should be low self-noise electrode, and the voltage difference of electrode pairs should be small, so that the target signal is not overwhelmed by the self-noise of electrode. So all-solid-state Ag/AgCl electrode is the most appropriate choice.

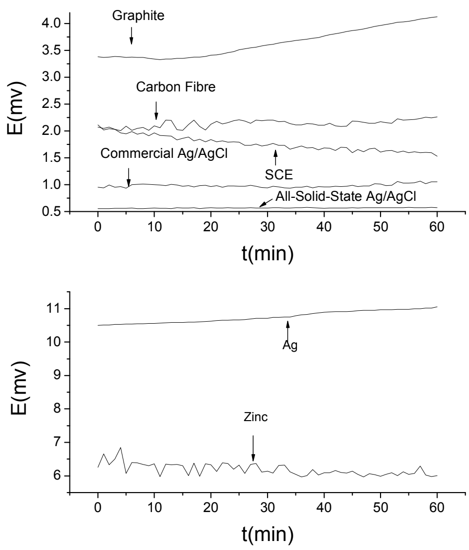

Fig.3 Voltage difference of electrode pairs

Conclusions

The DC resistance, the AC impedance and the voltage difference of Argent electrodes, zinc electrodes, graphite electrodes, carbon fibre electrodes, saturated calomel electrodes (SCE), all-solid-state Ag/AgCl electrodes and the Ag/AgCl electrodes bought from market were tested and compared, and the results of tests is that: the impedance of Argent electrode, saturated calomel electrode (SCE) and the Ag/AgCl electrode bought from market are large, which are not conducive to the measure of weak electric signal in marine environment. Although the impedance of zinc electrode is lower, the performance of it is unsteady, so it is not available for the detection too; the performance of all-solid-state Ag/AgCl electrode and carbon fibre electrode are excellent, and all-solid-state Ag/AgCl electrode is the best choice, by reason of that the resistance, impedance and voltage difference are smallest.

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