Preparation and Properties of Carbon Nanotube-Ag/AgCl Electrode for Marine Electric Field Test

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Abstract. The carbon dioxide was used as the material to modify the Ag/AgCl marine electric field electrode, and a new type of marine electric field detecting electrode was designed and manufactured. The surface morphology observation, electrochemical performance, electrode self-noise and range stability time were tested. The result shows that the specific surface area of the Ag/AgCl electrode increases greatly after the addition of carbon nanotubes and the range stability time is shortened. The range is small and the exchange current density become large. It shows good electrochemical performance. However, its electrode self-noise is too large, which is not suitable as a marine electric field detecting electrode.

1. Introduction
There are rich electric field signals in the ocean. Measuring ocean electric field for marine geological exploration is one of the main methods to research seawater flow[1], seabed geological structure, seabed mineral reserves and marine organisms. Just like the terrestrial electric field, the ocean electric field spread through contact. Seawater is a weak electrolyte. In seawater, electric current spreads through the form of ion motion. The lower the signal transmission frequency, the smaller the energy attenuation. Because the spread distance of the ocean electric field is so far that the main measured ocean electric field signals are low frequency and very low frequency. The signal strength of the ocean electric field is weak, generally uV level and the measurement period of the ocean electric field detecting electrode is long. The marine environment is so complicated that it requires the ocean electric field detecting electrode should have not only low self-noise and high structural strength, but also long-term stability and high measurement sensitivity[2].

At present, the main marine electric field detecting electrode is Ag/AgCl electrode. The Ag/AgCl electrode is convenient to use and can withstand large pressure so it is suitable for working in the marine environment. The Ag/AgCl electrode has excellent frequency response, low self-noise, stable potential, high measurement sensitivity, which means that it is an ideal choice for preparing marine electric field electrodes. Ag/AgCl electrodes have achieved great development[3–4]. However, the Ag/AgCl electrodes currently used still have some disadvantages that they need a long time to arrive at stability and have large range. Besides, they cannot deploy and measure quickly.

The manner in which the Ag/AgCl electrodes maintain stability of its range is that some electrochemical reactions occur on the surface of the electrode. When the reaction equilibrium is reached, the electrode potential reaches a steady state.

Therefore, the speed at which the reaction reaches equilibrium directly determines the time at which the Ag/AgCl electrode reaches stability. The speed at which the reaction reaches equilibrium is
directly related to the specific surface area of the electrode. The larger the specific surface area of the electrode, the higher the contact degree of the interface which will lead to the faster reaction and the shorter time for the electrode to reach the range stable state. Therefore, adding a component which can increase the specific surface area of the electrode and do not react with the electrode itself to improve the stability of the electrode potential, thereby shortening the range stable time is so reasonable.

Carbon materials such as carbon nanotubes have very good electrical conductivity and thermal conductivity. Some carbon materials have a porous surface and a high specific surface area which can greatly increase the contact area with the environment medium. At present, carbon materials have not only been widely explored and applied in the field of electrochemistry such as supercapacitors, electrocatalysis and solar battery, etc[5-6], but also been carried out in the field of related marine electric field detection[7]. Therefore, carbon nanotubes in carbon materials are undoubtedly worthy of trial. By introducing carbon nanotubes into Ag-AgCl powder and obtain the electrode after some process. The properties of the electrode are characterized by a variety of methods to investigate the effects of the carbon nanotubes on the properties of Ag/AgCl electrodes.

### 2. Electrode preparation

Firstly, the carbon nanotubes were pretreated. Then mixed the carbon nanotubes powder with Ag/AgCl powder according to the design ratio and fully ground to ensure uniform dispersion. After granulation, pressing and molding, the electrode body was obtained and then assembled to obtain an electrode sample. Carbon nanotube-Ag/AgCl electrode was obtained.

### 3. Electrochemical test

The exchange current density is a very important indicator of the stability of the reaction electrode in seawater. The higher the exchange current density, the better the stability of the electrode. The polarization curves of the prepared electrodes were tested by using a ZAHNER ENNIUM electrochemical workstation. This measurement used a three-electrode system in which the reference electrode was a calomel electrode and the auxiliary electrode was a platinum electrode.

The electrode’s Tafel curve was tested and the result is shown in Fig. 1. According to the definition of exchange current density i0, by TAFEL curve extrapolation method, under the equilibrium potential of the electrode. The current at this time is the exchange current density of the electrode. According to the Tafel formula:

\[
\eta = - \frac{2.303RT}{\alpha n F} \ln \left( \frac{i}{i_0} \right) + \frac{2.303RT}{\alpha n F} \ln \left( \frac{i}{i} \right)
\]

(1)

The exchange current densities of the Ag/AgCl and carbon nanotube-Ag/AgCl electrode samples were calculated respectively $3.98 \times 10^{-4}$A.cm$^{-2}$ and $3.14 \times 10^{-3}$A.cm$^{-2}$. It can be seen that the exchange current density of the carbon nanotube-Ag/AgCl electrode is about an order of magnitude higher than that of the Ag/AgCl electrode. It shows that the exchange current density of the Ag/AgCl electrode is significantly improved after the carbon nanotubes are added. This is because the addition of carbon nanotubes increases the specific surface area of the electrode, resulting in an increase in the number of ions per unit area and unit time. The higher the exchange current density, the better the electrochemical performance of the electrode itself. Therefore, the addition of carbon nanotubes contributes to the electrochemical performance of the Ag/AgCl electrode while the electrochemical properties are mainly related to the microstructure of the electrode surface.
4. Detection performance test

4.1 Range stable time
This measurement used a two-electrode system and the prepared Ag/AgCl electrode pair were respectively placed in 3.5%NaCl solution. The distance between the two electrodes was 25 cm and the measurement time was 24 hours. The range of the Ag/AgCl electrode electrode pairs was measured by a MASTECHMS 8050 benchtop digital multimeter.

![Graph 1: Electrode polarization curve](image1)

Fig. 1 Result of Electrode polarization curve

The measurement result is shown in Fig. 2. It shows that the range stability time are 24h (Ag/AgCl) and 6h (carbon nanotubeAg/AgCl). This indicates that the range stable time of Ag/AgCl electrode shorten obviously with the addition of carbon nanotubes, which makes Ag/AgCl electrode meet the needs of rapid deployment of marine electric field electrodes. The range difference of the electrodes are 1.2 mV (Ag/AgCl) and 0.2 mV (carbon nanotube-Ag/AgCl). The addition of the carbon nanotubes also reduces the range of the electrode, which increases the stability of the electrode. This is because the addition of carbon nanotubes increases the specific surface area of the electrode so the contact area between the electrode and the medium increases. The number of effective ion collisions increases and the number of ions that react at the same time increase. That is the reason why the time for the reaction to reach equilibrium is reduced and shortened so that the range stable time is shortened.

![Graph 2: Range drift of Ag/AgCl electrode](image2)

Fig.2 Range drift of Ag/AgCl electrode

4.2 Self-noise test
Electrode self-noise is an important indicator of the electric field detecting electrode. If the electrode is too noisy, it will cause glitch distortion in the response electric field waveform. The test used a two-electrode system and used the Sa200F3 low-noise amplifier whose magnification was 100 times to amplify the signal. The data was collected and recorded by using the MPS140401 data acquisition...
card. The measurement time was 2000s and the sampling interval was 0.008s. The electrode self-noise was obtained by performing Fourier transform on the measurement result.

Fig. 3 shows the self-noise measurement results of Ag/AgCl electrodes and carbon nanotube-Ag/AgCl electrodes. It can be seen from the test results that the self-noise of the Ag/AgCl electrode is 2.2nV/√Hz and the self-noise of the carbon nanotube-Ag/AgCl electrode is 10nV/√Hz so the self-noise level of the carbon nanotube-Ag/AgCl electrode at 1Hz is much large which is five times larger than the Ag/AgCl electrode. Excessive noise may affect or even covered the useful signal during actual use because it will have a great impact on the detection result so that it is difficult to meet the needs of ocean electric field detection.

5. Surface topography test

5.1 Electrode metallographic analysis
Metallographic analysis is an important mean of conducting electrode surface research. This experiment used a VHX-5000 metallographic microscope with a magnification of 500 times. Figure 6 shows the observed metallographic diagram.

As shown in Fig.4, the surface morphology of the Ag/AgCl electrode and carbon nanotubes-Ag/AgCl electrode are quite different. The surface of the Ag/AgCl electrode is very flat and the surface composition of the electrode is uniform. Therefore, the specific surface area of the electrode is limited, which can limit the electrochemical performance. However, the surface of the carbon nanotube-Ag/AgCl electrode is rough. There are many small pores and a large smooth area which is due to the agglomeration under the intermolecular force when the small particle size carbon nanotubes are mixed and dispersed in the Ag/AgCl powder. A network structure is formed inside the electrode. Because the carbon nanotubes have good electrical conductivity, the conductivity of the electrode is improved and the number of ions reacting at the same time inside the electrode is increased. As a result, the stability of the electrode can be improved significantly.

6. Conclusion
After testing and comparing the performance of carbon nanotube-Ag/AgCl electrode and Ag/AgCl electrode, it can be found that after adding carbon nanotubes, the specific surface area of the electrode of Ag/AgCl electrode is increased and the stability of the electrode is significantly improved. Both the
range stable time and the range of the Ag/AgCl electrode reduce. The exchange current density is greatly improved so that the electrode exhibits better electrochemical performance. However, the carbon nanotube-Ag/AgCl electrode has large self-noise, reaching 10nV/√Hz, which may mask the useful signal and thus is not suitable as a marine electric field detecting electrode.

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