

# The electrochemical behaviour of an exfoliated graphite electrode in simulated seawater containing oil

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**Abstract** An exfoliated graphite (EG) electrode was prepared and the electrochemical response to oil in simulated seawater was studied by means of the potential step technique and electrochemical impedance spectroscopy (EIS). The capacitance and other electrochemical characteristics of the electrode were affected by the presence of oil. The effects of temperature and salinity on the electrochemical behaviour of the EG electrode in NaCl solution containing oil were investigated by EIS. The results showed that the higher the temperature or the salinity, the higher the double layer capacitance of the electrode.

**Keywords** Exfoliated graphite · Oil · Seawater · Potential step technique · Electrochemical impedance spectroscopy

## 1 Introduction

Exfoliated graphite (EG) has attracted increasing attention as an oil-sorption material because of its large and special pore structure and hydrophobic surface characteristics. It has been found that EG can adsorb not only pure oil, but also oil in water, including floating oil and oil emulsions with water [1–6]. Its adsorption properties are even superior to those of PV-02 (a kind of polypropylene), which is a common oil-adsorbing material. Taking gasoline as an example, the EG adsorption amount is  $39 \text{ g g}^{-1}$  in 10 s, while that of the PV-02

is  $20 \text{ g g}^{-1}$  in 8 s [2]. For heavy oil, the sorption capacity is usually higher. Toyoda [5] investigated the sorption properties of different heavy oils and found that the capacities are 60–80 g per g of EG in a relatively short time, and the sorption capacity depends on the characteristics of the EG, while the sorption rate, as well as the sorption capacity, depends on the grade of heavy oil.

EG is usually prepared by rapid heating at about 1000 °C of a graphite intercalation compound, which is made of natural flaky graphite through chemical or electrochemical intercalation with sulfuric acid or acetic acid anhydride, etc. The intercalate is decomposed and volatilized instantly with a huge unidirectional expansion of the graphite flakes along the *c* axis and splitting of the graphite sheets [7–10]. The exfoliation ratio, which is calculated from the volumes of graphite particles measured before and after exfoliation, is an important characteristic of EG. The morphology of EG particles is worm-like and can be described by a zigzag model [7]. On a lump of EG, there are at least three kinds of pores: inter-particle pores, cleavage-like pores on the surface and intra-particle pores inside the particles. The large inter-particle pores are responsible for the sorption capacity of heavy oils with the cleavage-like and intra-particle ones assisting the capillary pumping [11]. Zheng [6] investigated the sorption capacity of EG for kerosene, vacuum pump oil and heavy oil. The results indicated that low viscosity oil was predominately adsorbed into worm-like particles, while high viscosity oil was more significantly retained in the space among worm-like particles.

Since oil spillage accidents in the marine environment occur frequently and cause serious environmental problems, it is necessary to find simple and fast methods for oil detection. Therefore, it is of significant interest to explore the oil-adsorbing property of EG as an electrode material for detecting oil in seawater, because EG preserves some of the

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electrical conductivity of graphite and seawater is a very good electrolyte solution. In the present work, an EG electrode was designed and vacuum pump oil was chosen to investigate the EG electrode response in simulated seawater. The effects of temperature and salinity of the simulated seawater on the electrode behaviour are also discussed.

## 2 Experimental

### 2.1 Preparation of electrodes and oil-containing simulated seawater

The working electrode was prepared using Ni foam as the substrate. An EG powder with exfoliation ratio of 150 and passing 325 mesh was used as the electrode active material. To prepare the electrode, polytetrafluoroethylene (PTFE) emulsion was added as a binder to the EG powder. After mixing, the paste was coated onto the Ni foam substrate. After drying, the electrochemical experiments were carried out in a 3-electrode test cell. A larger piece of Ni foam plate was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference.

A vacuum pump oil with kinetic viscosity of 93.0 mPa s was used. 3.5 wt.% NaCl solution containing the oil was prepared as oil-containing simulated seawater. The accurate concentration of the oil was measured by UV spectrometer.

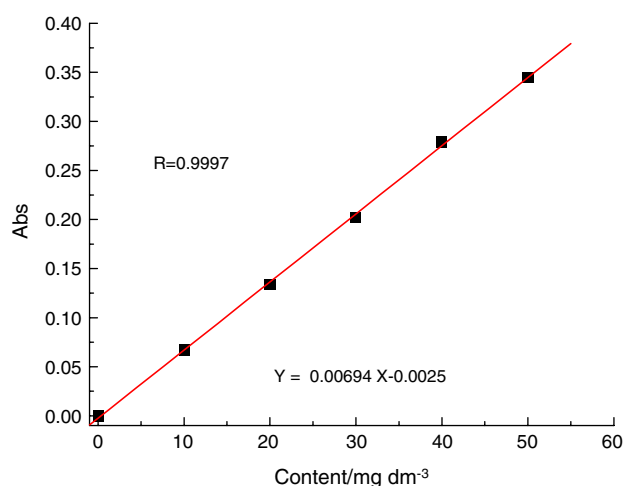
### 2.2 Electrochemical measurement

Potential step technique and electrochemical impedance spectroscopy (EIS) were carried out using an IM6E (Zahner Elektrik) to investigate the electrochemical response of the EG electrode. For the potential step technique, a step of 20 mV was applied in the non-faradaic window to detect the effect of oil on the electrochemical capacitance. For EIS, the potential perturbation was  $\pm 10$  mV and the frequency range was 10 mHz–100 kHz. An equivalent circuit was obtained for the electrode process with EQUIVCRT.PAS software, which reflected the different electrochemical characteristics of the electrode in the NaCl solutions with and without oil.

## 3 Results and discussions

### 3.1 Determination of the oil in simulated seawater by UV spectrometry

The content of the oil in the oil-containing simulated seawater was determined by UV spectrometry. A linear relationship between the absorbancy and the concentration



**Fig. 1** Standard curve for vacuum pump oil in *n*-hexane of UV spectrometry

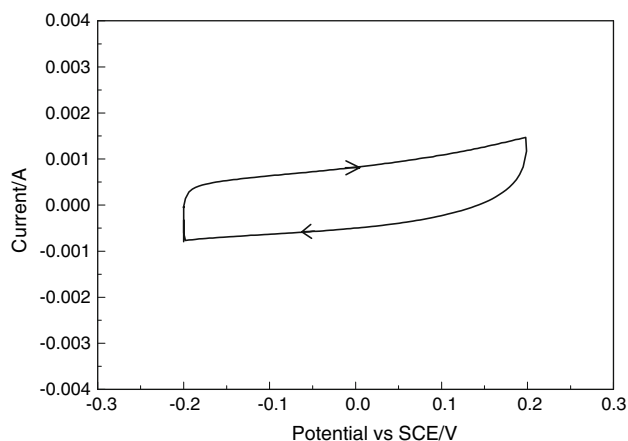
can be obtained at the maximum absorption wave-length of 225 nm on the basis of the Lambert-Beer law.

Figure 1 shows the standard curve for the vacuum pump oil. The solvent was *n*-hexane. To determine the oil content in the simulated seawater, the oil was first extracted by means of vigorous shaking in *n*-hexane, then the absorbancy was measured and the concentration was determined according to the standard curve. The result was 6.2 mg dm<sup>-3</sup>.

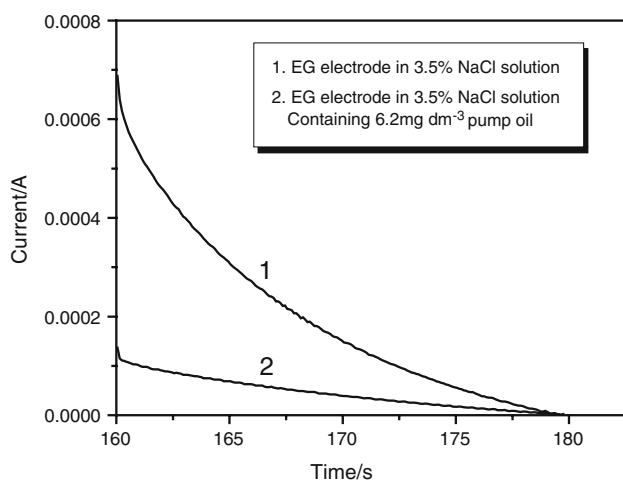
### 3.2 Potential step response

The electrical conductivity of oil is poor as compared to NaCl solution. If some oil is adsorbed in the EG electrode due to the oil-adsorption properties of EG, the electrode capacitance will be changed considerably, which can be measured by the potential step method. In a non-faradaic process, the behaviour of an electrode-solution interface is analogous to that of a capacitor. When a potential step is applied to the electrode, the flowing current corresponds to the double layer charging. Thus, the capacitance may be expressed as  $C_d = \Delta Q / \Delta \phi$ , where  $\Delta Q$  is the charge of the double layer on the potential step  $\Delta \phi$  [12]. The complete charging of rough surfaces makes this technique appropriate for porous electrodes.

Figure 2 shows the cyclic voltammogram (CV) behaviour of the EG electrode in 3.5 wt.% NaCl solution. The open circuit voltage (OCV) was  $-166$  mV (vs. SCE). It can be seen that reaction current was absent in the  $-200$  mV to  $+200$  mV range (vs. SCE). Therefore, a potential step of  $+20$  mV from the OCV was employed to measure the electrode capacitance. It should be noted that, both charging and faradaic currents were detected for the electrode in the oil-containing solution, although the former was predominate, due to high surface area of EG and its sensitivity to impurities in the oil. The *I*-*t* curves upon the



**Fig. 2** Cyclic voltammogram of the EG electrode in 3.5 wt.% NaCl solution (scan rate:  $20 \text{ mV s}^{-1}$ )



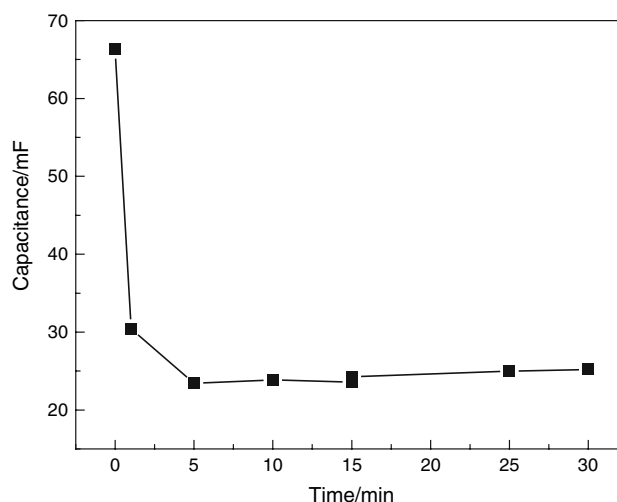
**Fig. 3** Current–time curves obtained from potential step for the EG electrode in NaCl solutions with and without vacuum pump oil

step for the electrode in the NaCl solutions with and without oil are shown in Fig. 3. The micro background faradaic current was deleted in the case of curve 2.

As seen in Fig. 3, the charge capacity for the capacitance of the electrode in NaCl solution was much larger than that of the electrode in the solution containing  $6.2 \text{ mg dm}^{-3}$  oil. Based on the equation of  $C_d = \Delta Q / \Delta \phi$ , for the electrode in the oil-containing and oil-free solutions, the  $C_d$  values were calculated as  $0.0443 \text{ F}$  and  $0.196 \text{ F}$  respectively.

### 3.3 Effect of adsorption time

The sorption rate is important for practical applications of the EG material. In order to determine the response of the EG electrode in a NaCl solution containing oil, it is essential prior to testing to find the proper immersion time of the electrode required to reach the adsorption



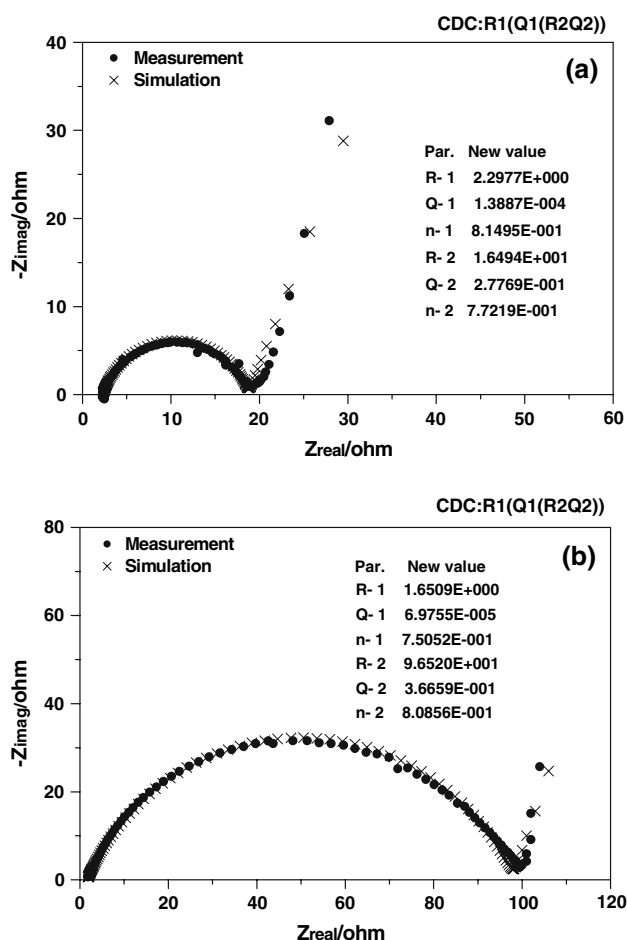
**Fig. 4** Effect of immersion time on the capacitance of the EG electrode in 3.5 wt.% NaCl solution containing  $6.2 \text{ mg dm}^{-3}$  vacuum pump oil

equilibrium in the oil-water medium. The effect of time on the oil adsorption amount in the electrode was investigated by the capacitance data obtained from the potential step method, as shown in Fig. 4.

It can be seen clearly that the adsorption process was very fast at the beginning. The capacitance decreased to the minimum within 5 min and then changed very little with time. Therefore, in our case, the measurements were carried out after immersing for 10 min.

### 3.4 EIS characteristics

The electrochemical behaviour of the EG electrode in NaCl solution containing oil was also investigated by EIS. The perturbation was  $10 \text{ mV}$  and the frequency range was from  $10 \text{ mHz}$  to  $100 \text{ kHz}$ . The impedance spectra and the simulated data of the electrode in the NaCl solutions with and without oil are presented in Fig. 5. The proposed equivalent circuit is illustrated as a Randles model- $R1(Q1(R2Q2))$ . Q terms represent constant phase elements (CPE). R1 is the electrolyte resistance. The semi-circle in the higher frequency range (R2Q1) is assigned to a charge transfer process. Q1 symbolizes the CPE related to double layer capacitance of the active surface of the EG electrode. Q2 is associated with the diffusion process of the reaction in the electrolyte. The values of the elements are also shown in Fig. 5. Obviously, in the solution containing oil, Q1 was lower than that of the electrode in the solution without oil, which was in agreement with the result from the potential step method. Q2 of the electrode in the oil-containing solution was somewhat high as compared with the value of the electrode in oil-free solution. In addition, the reaction resistance R2 increased by several fold due to



**Fig. 5** Electrochemical impedance profiles of the EG electrode in 3.5 wt.% NaCl solution (a) and 3.5 wt.% NaCl solution containing 6.2 mg dm<sup>-3</sup> vacuum pump oil (b)

the presence of oil in solution, which could indicate that the oil adsorbed in EG covered some active sites and inhibited the electrochemical reaction.

### 3.5 Effects of temperature and medium salinity on the electrochemical behaviour

The effects of temperature and salinity on the electrochemical behaviour of the EG electrode in NaCl solution containing oil were investigated by means of EIS. New electrodes were prepared and used in the study of the two effects, respectively.

#### 3.5.1 Effect of temperature

Table 1 shows the results obtained from the EIS of the electrodes in NaCl solution containing 6.2 mg dm<sup>-3</sup> oil at different temperatures. It was found that the double layer capacitance increased with increasing temperature. For the oil-containing medium, there are two competitive

processes, namely, the oil dispersion in the aqueous solution and oil adsorption on the EG electrode. Higher temperature favors oil dispersion in water and results in reduced oil adsorption on EG. Therefore, the capacitance of the EG electrode increased with temperature.

In addition, as seen in Table 1, it can also be concluded that the temperature had little effect on the reaction resistance and the diffusion impedance of the EG electrode.

#### 3.5.2 Effect of salinity

NaCl dissolved in water containing oil has agglomerative effect on oil dispersion process, which influences the electrochemical performance of the EG electrode. The behaviour of the EG electrode in the media containing 6.2 mg dm<sup>-3</sup> oil and NaCl with concentrations of 2.0, 2.5, 3.0 and 3.5 wt.% was investigated and discussed. The results are presented in Table 2.

The electrode capacitance increased with salinity, which suggested that the adsorption capacity of oil in the EG electrode decreased. This trend became increasing obvious at high salinity. It is possible that the agglomerative effect results in aggregation of oil phase into larger droplets, which prevents their access into the pores of the EG electrode, especially at high salinity. Therefore, at high salinity, the capacitance of the electrode increased significantly.

**Table 1** Equivalent circuit elements data for the EG electrode in 3.5 wt.% NaCl solution containing 6.2 mg dm<sup>-3</sup> vacuum pump oil at different temperatures

Temp/ °C	20	30	40	60
R1/Ohm	1.135	0.9921	0.9103	0.7447
CPE1/ $\mu$ F	97.74	147.0	181.4	231.2
n1	0.7243	0.7459	0.7554	0.8190
R2/Ohm	44.55	49.34	57.85	70.44
CPE2/mF	256.9	266.9	351.7	426.8
n2	0.7991	0.7579	0.8048	0.7958

**Table 2** Equivalent circuit elements data for the EG electrode in different NaCl solutions containing 6.2 mg dm<sup>-3</sup> pump oil at room temperature

NaCl /wt. %	2.0	2.5	3.0	3.5
R1/Ohm	2.495	1.974	1.883	1.792
CPE1/ $\mu$ F	87.40	98.87	148.7	209.1
n1	0.7417	0.7481	0.6899	0.6899
R2/Ohm	72.87	75.26	70.60	89.14
CPE2/mF	244.5	345.2	294.9	197.3
n2	0.8059	0.8910	0.9445	0.6862

#### 4 Conclusions

- 1) As compared with 3.5 wt.% NaCl solution, the double layer capacitance of the EG electrode is reduced in the solution containing vacuum pump oil. When the EG electrode was immersed in the oil-containing solution, the capacitance decreased to a minimum within 5 min, then changed very little with time, indicating fast adsorption rate. Potential step technique is a suitable method to measure the capacitance.
- 2) The equivalent circuit for the EG electrode in simulated seawater is described well by the Randles model- $R_1(Q_1(R_2Q_2))$ . The element data for the EG electrode in NaCl solution containing oil changed significantly as compared to those of the EG electrode in the oil-free solution.
- 3) The EIS results showed that the double layer capacitances of EG electrode increased significantly with increase of temperature or salinity of the oil-containing medium because the adsorption capacity of oil in the EG decreased.

It may be concluded that the electrochemical response of the EG electrode is sensitive to the presence of oil in simulated seawater and, therefore, it is a highly promising, simple and fast method for oil detection in seawater.

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