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*Short Communication*

# Preparation of Graphene-Cement Paste Anode for Chloride Extraction from Marine Reinforced Concrete Structures

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Electrochemical chloride extraction (ECE), a technology for the rehabilitation of chloride-contaminated concrete, has attracted widespread attention. The performance of the ECE method towards marine reinforced concrete was studied with the graphene-cement paste as anode and artificial sea-water as electrolyte. The efficiency of removing chloride obtained with graphene-cement anode was higher than that obtained with a conventional Ti-$RuO_2$ mesh anode. With the usage of the graphene-cement anode, the chloride extraction process was found to be more effective for the surface area. In addition, the performance of ECE process was also investigated by altering various parameters such as moistening frequency and current density. The results demonstrated that every 12 h drip moistening system was necessary in order to maintain the constant humidity, and further constant performance.

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**Keywords:** Electrochemical chloride extraction; Graphene-cement; Moistening; Ti-$RuO_2$;

## 1. INTRODUCTION

Corrosion of reinforcing steel bars, regarded as the well-known cause for the degradation of reinforced concrete structures, have attracted intense attention from the whole world. Initially, the alkaline solution in the pore of steel can protect the embedded steel in concrete from corrosion [1, 2]. Owing to this high alkalinity, a passive film was formed on the rebar surface which hindered the appearance of the active corrosion process. However, the passive film which hampered the corrosion process can be destructed by the entering aggressive ions (e.g., chlorides and sulfates) or carbonation (i.e., acidification of the surroundings near the rebar). In marine environment, the corrosion of reinforcing steel is naturally resulted from the penetration of chloride in reinforced concrete. Under the condition of entering chloride, the depassivation of steel rebars occurred and subsequently a porous oxide layer at the steel-concrete interface formed. Unfortunately, the volume of the formed iron oxides layers was 2-4 times higher than that of iron, which generated stress within the concrete. Furthermore, the developed stress can lead to certain irreversible damages (e.g., the crack of concrete and the loss of carrying capacity) to the structure and finally destroy the structure completely [3-5].

Electrochemical chloride extraction (ECE) is a method to remove the harmful chloride ion in the concrete. The ECE technique has many advantages, such as easy conduction, high efficiency and low cost. Most importantly is that the ECE technique was carried out without destroying the structure of the concrete. When conducting the ECE experiment, a certain external electric field was applied and thus the passivation in the concrete surface was repaired and reactivated. In the 1970s, Federal Highway Administration developed the electrochemical chloride extraction technology for the first time, and then the experiments conducted by the ECE method were carried out in two states of USA (Ohio and Kansas) [6]. After that, a large number of related studies were appeared in European and USA [7]. The new method was proved to be time-saving and cost-effective. Therefore, a company named Norcure had applied for a patent on this new technology in 1988, and since then the technology was named Norcure$^{TM}$ [8]. After applying the patent, the ECE technology was used successfully for repairing the Burlington highway in Ontario of Canada firstly. Afterwards, the ECE method obtained a wide range of usage all around the world (e.g., German, North Europe and North American) from 1987 to 1998. In addition, the repair area up to 182,000 m$^2$ was finished according to the statistics given by the Norcure company [9]. Moreover, the ECE technology was established as the national norm in Europe (1994), Norway (1995) and British (2000) as well [10].

Although the ECE technology was widely used, it was still underdeveloped. In the application of the technology, there was still a great deal of problems to be solved. For example, the invention of a suitable anode was highly required for the ECE process. Owing to its structure durability and ultimate mechanical strength, the cementitious materials have played an important role in structural engineering. Recently, a lot of studies have been carried out to develop further functionalities of this material for expanding its application [11]. Fortunately, as revealed by the experiments done by Pérez and co-workers, the concrete specimens in the laboratory scale could be repaired using the ECE method with a anode made of conductive cement [12].

The cement-based materials can be divided into many categories, of which the electrically conductive materials attracting great concerns. Generally, the electrical conductivity of regular concrete is extremely poor, which makes it hardly used as an electrode. An effective method for solving the conductive problem is to add some conductive materials (e.g., graphite powder and carbon fibres) into concrete [13-16]. The as-prepared composite, characterized with special properties both in chemical and physical, has been a promising candidate for manufacturing certain advanced products. Except the above-mentioned conductive materials, the graphene nano-platelet (GNP) as carbon-based material in nano-scale was put forward and attracted more and more attention now. Owing to many advantages such as good mechanical properties and low cost, GNP has found an increasingly wide utilization in the production of polymer or cement nanocomposites till now [17-20].

In our work, GNP powder was used for prepare conductive cement paste and then the as-synthesized material was utilized in constructing the anode for the ECE technology. Then the structure of marine reinforced concrete was analysed using the constructed ECE device. Several ways of decreasing the amount of anode material were tried for material saving, and further cost saving in the real applications of the ECE method.

## 2. EXPERIMENTS

### *2.1 Materials and Specimen Preparation*

The dosages of the produced concrete mix were shown in Table 1. Firstly, ordinary cement (Portland) with limestone (CEM II/B-L 32.5 N) was mixed together, after that certain NaCl at a ratio of 2% referred to the cement mass was added. Then the mixture was casted and demould lastly. Before use, the mortars were placed into a standard curing chamber for nearly 1 month. The steel rebars (HRB 335) with the chemical compositions shown in Table 2 were embedded into the as-prepared concrete. The diameter of the used steel rebars was 8 mm. The concrete cover was in the thickness of 4 cm.

**Table 1.** Dosages and characteristics of the concrete mix.

| Materials or properties | Concrete |
|---|---|
| Cement (kg/m$^3$) | 150 |
| Distilled water (kg/m$^3$) | 150 |
| Limestone sand (kg/m$^3$) | 650 |
| Plasticizer (kg/m$^3$) | 1.22 |
| NaCl (kg/m$^3$) | 3 |
| Water/cement ratio | 1 |

**Table 2.** Chemical compositions of steel rebar (wt.%).

| C | Si | Mn | Cr | Mo | Ni | Cu | S |
|---|---|---|---|---|---|---|---|
| 0.34 | 0.05 | 0.35 | 0.67 | 0.12 | 0.02 | 0.12 | 0.09 |

### *2.2 Anodes preparation*

The graphene-cement anode was prepared by homogenously mixing cement, graphite powder and water with the weight ratio of 1:1:1.6, respectively. For the sake of avoiding the entering of chloride ions, the graphene-cement anode was made into a layer with the thickness of 2 mm after treatment. The titanium-ruthenium oxide was used as the reference anode and its electric resistance is 0.041 Ω/m. The SEM images of GNP at different magnifications were shown in Fig. 1.

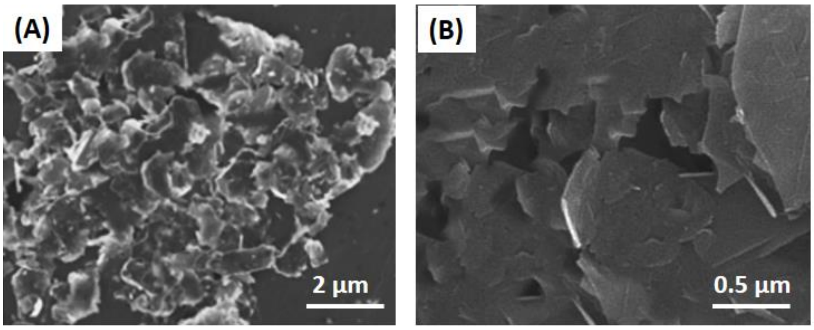

**Figure 1.** SEM image of graphene nano-platelet under (A) low and (B) high magnificantions.

### *2.3 Electrolyte and ways of moistening*

In order to evaluate the application of ECE technology for repairing the structure of marine reinforced concrete, the artificial seawater whose compositions shown in Table 3 was synthesized as the electrolyte. In the process of ECE technology, constant humidity is required. Therefore, three different moistening methods including constant or every 2h drip moistening system and daily dampening system were used for achieving constant humidity in our work.

**Table 3.** The compositions of artificial seawater.

| Salt | Amount (g/kg) |
|---|---|
| NaCl | 23.926 |
| $Na_2SO_4$ | 4.008 |
| KCl | 0.677 |
| $NaHCO_3$ | 0.196 |
| KBr | 0.098 |
| $H_3BO_3$ | 0.026 |
| NaF | 0.003 |

### *2.4 Electrochemical chloride extraction process*

The ECE process was carried out in plastic reservoirs with a titanium mesh wrapped external anode. A maximum current density of 2~6 A/cm$^2$ and the maximum possible extraction voltage of 40 V were used for ECE process. The whole ECE process was carried out for 28 days.

### *2.5 Chloride analysis determination*

The potentiometric titration was explored to determine the concentration of acid-soluble $Cl^-$ in the concrete samples. The concentrations of $Cl^-$ in concrete or graphene-cement anode referred to the content of acid-soluble chlorides in our work. And the concentrations were expressed as percentages relative to cement mass and total mass in the case of concrete and graphene-cement anode, respectively. By integrating the profiles of $Cl^-$ content, the amounts of chloride involved in both concrete anode and graphene-cement anode can be obtained before and after the ECE process, which allowed the calculation of the efficiency of the ECE technology for decreasing the content of chloride in concrete.

## 3. RESULTS AND DISCUSSION

The micrographs of the graphene-cement paste were characterized with SEM using backscattered electrons and the results were shown in Fig. 2. Obviously, graphene sheets with a winkle structure could be observed.

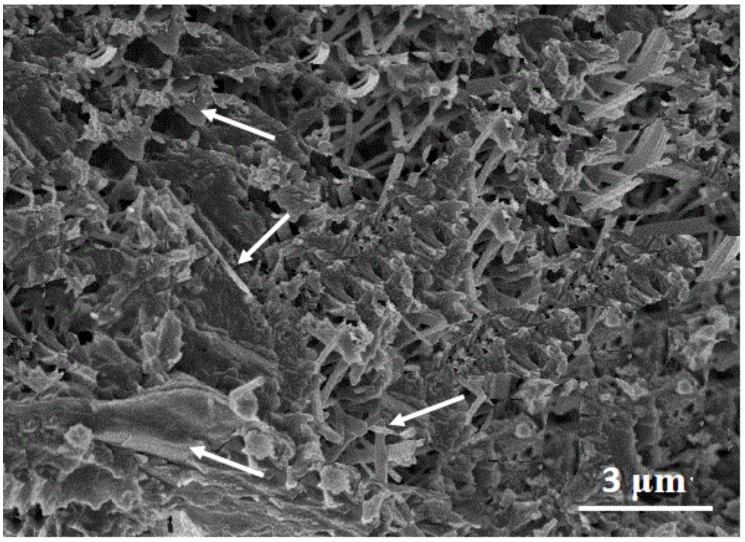

**Figure 2.** SEM image of the graphene-cement paste

The concentration profiles of chloride in the marine reinforced concrete obtained with the ECE process using Ti-$RuO_2$ mesh anode and graphene-cement anode were shown in Fig. 3A and 3B, respectively. In this experiment, constant humidity was achieved by a constant drip moistening system. The initial concentration of chloride obtained from a specimen without ECE treatment and the final concentration of chloride after ECE treatment could be calculated from these figures. Subsequently, the local efficiency of the treatment could be achieved. As calculated from Fig. 3A, the average efficiency of ECE treatment with Ti-$RuO_2$ mesh as the anode was 79.4%, which corresponded to the content of $Cl^-$ extracted from the zone covered by concrete.

Customarily, the efficiency is critical to the application of the ECE technology. The average efficiency was 79.9% for the ECE process with the graphene-cement anode which was synthesized by replace 50 % cement with graphene nano-platelet powder. The efficiency obtained with graphene-cement anode (81.3 %) was slightly higher than that obtained with Ti-$RuO_2$ mesh (68.9 %), demonstrating the feasible usage of the graphene-cement composite in constructing anode for the ECE process. The local efficiencies achieved with the tested two anodes (graphene-cement anode and Ti-$RuO_2$ mesh anode) were compared and the results were shown in Fig. 3C. As revealed by Fig. 3C, when the graphene-cement anode was employed, much higher efficiency was achieved for the areas near the concrete surface. Pérez et al [21] have showed that a significant amount of chloride would retain on the surface of the anode after the ECE treatment. Fortunately, it is better in our experiment that negligible amount of chloride retained on the surface of the graphene-cement anode after the ECE process, owing to the high porosity composite after incorporating with GNP. Cañón and co-workers demonstrated the feasibility of employing an anode of sprayed conductive cement paste, based on a 50% replacement of cement by graphite powder [22]. The efficiency obtained with graphite-conductive cement anode is 79.2%, is almost the same to the one obtained by using a conventional anode (Ti-$RuO_2$ mesh), which is a 79.4%. This result is slightly higher than our proposed graphene-conductive cement anode. What's more important is that the graphene-cement anode could repair the structure of reinforced concrete continuously. In general, the proposed graphene-cement anode is suitable to be applied in various consecutive treatments, shielding of electromagnetic fields and cathodic protection as well. Besides, since the chloride extraction is more effective in the surface area in the case of using graphene-cement anode, the ECE treatment involving graphene-cement anode can be particularly applied in the following cases where the corrosion process is not very serious.

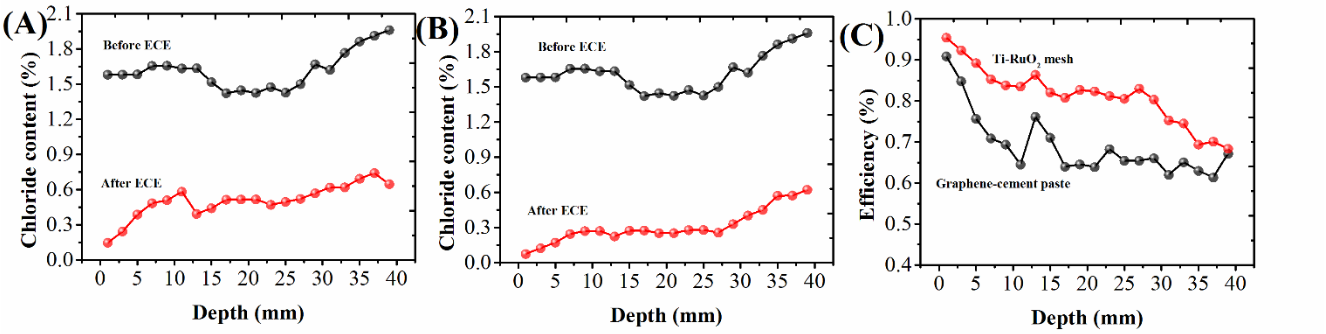

**Figure 3.** Chloride concentration profiles of the marine reinforced concrete before and after ECE process using (A) Ti-$RuO_2$ mesh anode and (B) graphene-cement anode. (C) Chloride removal efficiency comparison profiles.

All the experiments mentioned above were performed with the charge density of 6 $A/cm^2$. Herein, the efficiency of the ECE process with the graphene-cement anode was studied with different charge density. The chloride concentration profiles of the marine reinforced concrete after the ECE process using charge density of 4 $A/cm^2$ and 2 $A/cm^2$ was shown in Fig. 4A and Fig. 4B, respectively. As revealed by Fig. 4, when the applying charge density of 4 $A/cm^2$ and 2 $A/cm^2$ used, the average efficiencies of the ECE process with graphene-cement anode were 78.6 % and 67.3 %, respectively. The results obtained demonstrated the successful application for on-site testing by the ECE technology constructed with the proposed graphene-cement anode. Table 4 shows the comparison of the remove efficiency of our proposed anode with other reported literatures.

**Table 4.** ECE efficiency comparison of proposed anode with other literatures.

| Anode | Applied charge density | Time | Remove efficiency | Reference |
|---|---|---|---|---|
| Graphite-conductive cement | 5 MC/m$^2$ | 28 days | 79.2% | [22] |
| Carbon nanofibres-cement | 2 A/cm$^2$ | 139 h | 72.4% | [23] |
| Carbon-fiber-reinforced polymer | 3 A/cm$^2$ | 28 days | 80.39% | [24] |
| Graphene-conductive cement | 4 A/cm$^2$ | 28 days | 78.6% | This work |

It is well known that constant humidity is highly demanded during the ECE process. Owing to the increased electrical resistance of cementitious materials upon drying, the driving voltage was increased necessarily in order to maintain the constant current density [25, 26]. Therefore, as an anode, the ability to retain moisture is indispensable during the ECE treatments. Herein, three different system including constant or ever 2 h drip moistening and daily dampening were used for retaining humidity and the compared efficiencies were shown in Fig. 5A. During the entire experiment, the composite of graphene-cement was used as the anode and the current density applied was 6 A/cm$^2$. As shown in Fig. 5, there was basically no difference in the remove profiles of chloride no matter a constant or every 2 h drip moistening system was used.

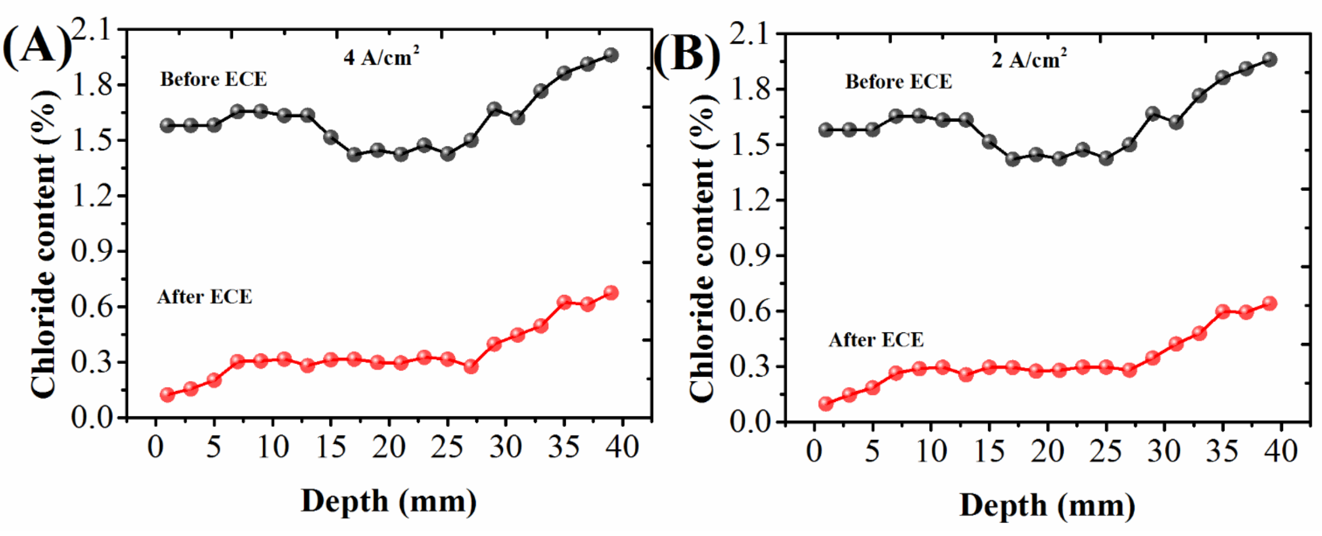

**Figure 4.** Chloride concentration profiles of the marine reinforced concrete before and after ECE process using graphene-cement anode at (A) 4 A/cm$^2$ and (B) 2 A/cm$^2$.

However, when the daily dampening moistening was used, the removal rate of the chloride exhibited an obvious decrease. In order to further understand the effect of the usage of a daily dampening moistening method, the feeding voltage was measured during the ECE process. As demonstrated in the Fig. 5B, the initial feeding voltage was about 12 V, and no observable change of the feeding voltage was found within the first 12 h, which indicated that a single dampening was enough to keep the moisture state constantly. However, the feeding voltage increased significantly after 12 h and eventually up to 44 V. This is because the conductivity of the electrolyte was decreased with the decreasing of moisture.

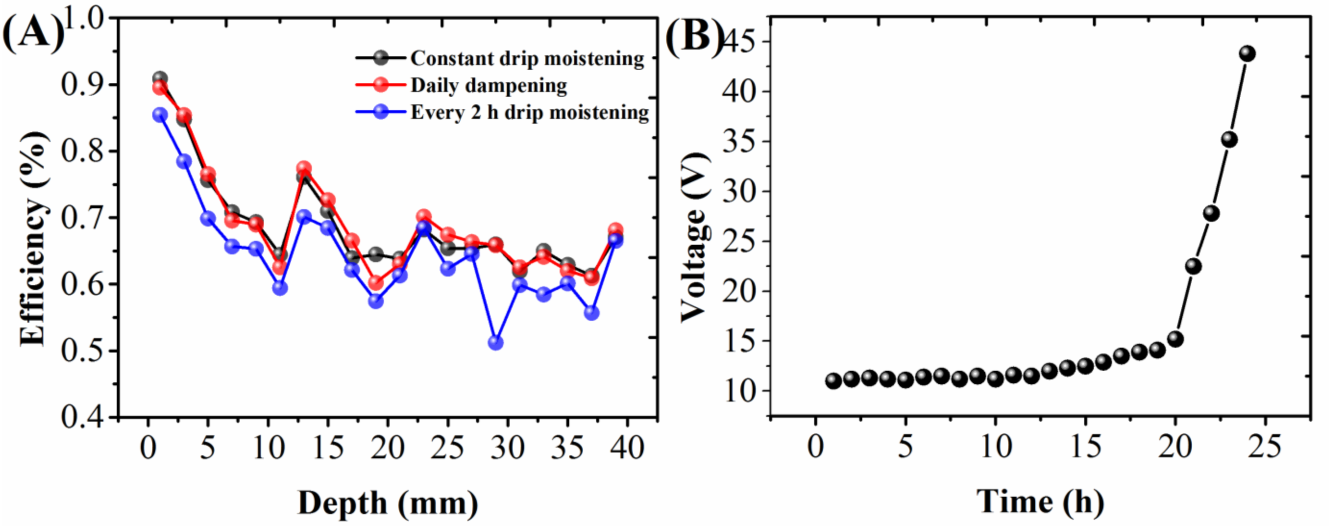

**Figure 5.** (A) Compared efficiencies of ECE treatments using a constant drip moistening system, a daily dampening and every 2 h drip moistening system. (B) Evolution of driving voltages in the ECE treatment using a daily dampening moistening mode.

If the surface was watered at this point, the voltage would return to the initial value approximately. In general, for the sake of the constant performance, every 12 h drip moistening system was necessary.

## 4. CONCLUSIONS

In conclusion, a graphene-cement anode composed of graphite powder and cement with weight ratio 1:1 was constructed for the ECE process. As revealed by the entire experiments, the graphene-cement anode exhibited slightly higher efficiency than the conventional Ti-$RuO_2$ mesh anode. When using the graphene-cement anode, the chloride extraction process is more effective for the surface area. Thanks to the capacity of the graphene-cement anode, the insert of chlorides was retained, which enabled the easily conduction of further treatments in the system. Besides, in the case of using graphene-cement anode, the moisture could be retained up to 12 h, which was of great importance for the utilization of ECE on site. The average efficiency obtained using ECE treatment with the graphene-cement anode was 71.4% when applying electric current of 4 $A/cm^2$.

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