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Monitoring chloride ion penetration in concrete structure based on the conductivity of graphene/cement composite

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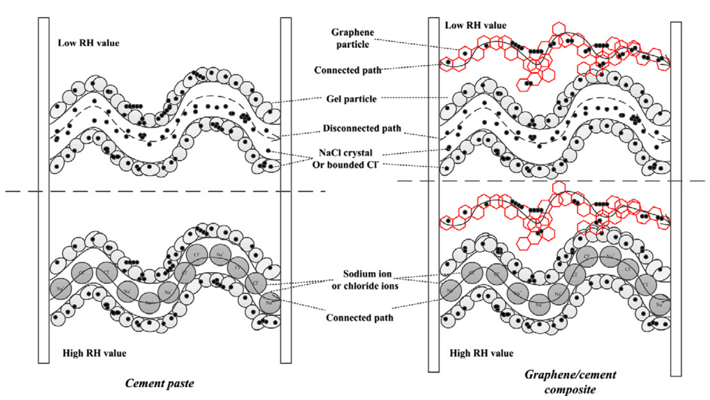
HIGHLIGHTS

- Graphene/cement composite could be applied as Cl^- sensor in concrete.
- The conductivity of graphene/cement composite was independent on the Cl^- content.
- Accurate measurement of conductivity of composite was obtained by EIS technique.
- Cl^- penetration in concrete was monitored by means of embedded composite.

GRAPHICAL ABSTRACT



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ABSTRACT

A non-destructive method of monitoring chloride ion penetration in concrete structure has been investigated by means of the conductivity of graphene/cement composite. The conductivities of cement paste and graphene/cement composite by incorporation of various chloride ion contents have been determined by EIS measurement at different RH values. Meanwhile, the micro-morphology and phase composition have been detected by SEM and XRD techniques, respectively. Besides, the chloride ion penetration in mortar paste has been monitored through embedded graphene/cement composite. Results revealed that the conductivity of graphene/cement composite increased with the increase of chloride ion content regardless of RH value because the electrical current passed through the networks formed due to contacts between graphene particles and generated by connected pore solution. Moreover, the real-time monitoring of chloride ion penetration in mortar paste can be achieved through measurement of the conductivity of embedded graphene/cement composite. In a word, graphene/cement composite provided a possibility of monitoring chloride ion erosion in concrete structure.

1. Introduction

Corrosion of reinforced steel in concrete was usually initiated due to the transport of chloride ion (Cl^-) from sea water or deicing salts, which is the major cause of degradation of concrete structures. The best ways to reduce the loss of corrosion-induced

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damage is through prevention, including monitoring the chloride ion penetration in concrete structure. A lot of field and lab techniques have been adopted to determine Cl^- concentration in concrete structure [1]. Among them, potentiometric and Volhard methods are mostly applied techniques by which free and total Cl^- contents of concrete can be obtained. However, these techniques are usually destructive and time-consuming [2]. What's worse, it is almost impossible to measure the real-time change of Cl^- content in concrete by means of these techniques.

Differing from the destructive techniques, non-destructive technique (NDT) has been highly respected to determine the chloride ion content in concrete for the reason that this technique produces no negative effects on the environment and further use of material where the detection is taken [3]. Moreover, the prediction of service life of concrete structure can be evaluated based on these NDT [4,5]. Currently, the NDT applied in measurement of chloride ion content in concrete structure include electrical resistivity [6,7], optical fiber [8–10] and chloride ion selective electrode [2,11–14]. Nevertheless, the complex conditions such as inhomogeneity, change in temperature, relative humidity and pH value in concrete cause severe interference on the accuracy of measurement.

Fortunately, these interfering factors has no influence on the measurement of Cl^- concentrations obtained by sensors fabricated based on the cement material for the reason that concrete belongs to cement-based material in nature. Kim [15] investigated the development of electrical conductivity of carbon nanotube/cement composite measured through direct current technique by addition of chloride ion and found out the conductivity of carbon nanotube/cement composite increased with the increase of chloride ion concentration. However, it usually took several hours for the conductivity measurement to reach the stable condition by means of the direct current technique. In addition, the polarization induced by direct current produced considerable effects on the results of measurement. Hence, elimination of these negative effects on measurement of conductivity would be achieved through AC technique [16,17]. Besides, recent advance in materials science and nanotechnology provided an excellent nanomaterial, i.e., graphene, which exhibited excellent properties such as high intrinsic mobility ($200{,}000\ cm^2\ v^{-1}\ s^{-1}$) and large theoretical specific surface area ($2630\ m^2\ g^{-1}$) [18–20]. The conductivity of cement paste would be improved in a significant degree with the addition of graphene [21]. However, few literatures have reported monitoring chloride ion content in concrete by mean of the conductivity of graphene/cement composite.

To evaluate the feasibility of applying the graphene/cement composite as the chloride ion sensor, cement paste and graphene/cement composite with addition of different chloride ion concentrations were fabricated and their conductivities at different relative humidity values (RH) were determined by electrochemical impedance spectroscopy (EIS) technique in the present work. Furthermore, the relationships between the conductivities of cement paste as well as graphene/cement composite and chloride ion contents have been established. Besides, the morphology and composition of cement paste and graphene/cement composite have been detected by scanning electron microscopy (SEM) and X-ray diffraction (XRD) technique, respectively. Moreover, the chloride ion penetration in mortar has been investigated based on the embedded graphene/cement composite.

2. Experimental

2.1. Materials and mix proportions

The cementitious material used in our work was P.II 42.5 (GB175-2007) Ordinary Portland cement (OPC), the oxide composition of OPC has been presented in Table 1. Purified Graphene produced by Hengqiu Graphene Technology Co., Ltd was applied in this investigation. The Graphene was produced by the oxidation-reduction method and their purity was higher than 90%. Their diameter and layers were in the range of 10–50 μm and 1–5 layers, respectively. Besides, the thickness for the graphene was between 10 and 1.77 nm and the single rate was more than 30%. The specific surface area of the graphene was in the range of $360–450\ m^2\ g^{-1}$. In addition, the polycarboxylate superplasticizer was incorporated in order to improve the workability of graphene/cement composites. The sodium chloride with 99% purity was used as chloride ion source and deionized water was used in the whole investigation.

The ratio of 0.5 was chosen as the ratio of water to cement. 1.0 cm × 1.0 cm × 3.0 cm specimens were cast with two different amounts of graphene, i.e., 0 and 2% by cement weight. The detailed mix proportions of graphene/cement specimens were shown in Table 2. To investigate the influence of chloride ion concentration on the conductivity of graphene/cement composites, chloride ion in amounts of 0, 0.01, 0.05, 0.1, 0.5, 1 and 3% by cement weight were added for each mixture. The graphene together with cement were mixed for 5 min in a commercial mixer before cast. Two pieces of stainless steel mesh electrodes (2.0 cm × 2.5 cm × 0.05 cm) were inserted into the specimen (approximately 3.0 cm electrode spacing) immediately after casting, the scheme for the graphene/cement specimen was shown in Fig. 1. After that, these specimens were demolded after 24 h. Then they were stored in the curing chamber (95% relative humidity, 25 °C) for 28 days.

The mortar paste with the water to cement ratio of 0.5 were cast in order to monitor the chloride ion ingress based on the embedded graphene/cement composites. The mass ratio between cement, water and fine aggregate in the mortar paste was 1:0.5:2.5. The river sand with a specific gravity of 2.60% and 0.45% water absorption was applied in our work. Moreover, the contact segment between the copper wire and the stainless steel mesh was sealed by means of epoxy resin. The diagram for the mortar paste was presented in Fig. 2.

2.2. Experimental details

2.2.1. Electrical conductivity tests of graphene/cement composites

After 28 days of curing, these graphene/cement composites were conducted with alternating current (AC) measurements. The AC measurement was carried out with EIS technique through a sinusoidal potential perturbation of 10 mV at the open circuit potentials with the frequency ranged from 10 mHz to 100 kHz by means of a Princeton Applied Research (PAR) START 2273 Potentiostat. 5 specimens were fabricated for every kind of situation in order to obtain reliable results.

Due to the reason that the resistance (R) was dependent on the geometry of specimen, the electrical resistivity (ρ) was applied to evaluate the electrical performance of the composite, which can be expressed by the following equation:

$$\rho = \frac{R \cdot A}{L} \tag{1}$$

where A and L are the cross-sectional area and the length of the specimen, respectively.

Furthermore, electrical conductivity (σ) of the specimen was calculated based on the resistivity:

$$\sigma = \frac{1}{\rho} \tag{2}$$

The EIS measurements for graphene/cement composites were performed in different relative humidity (RH), i.e. 0, 50, 70 and 90%, respectively. In order to make sure the completely dry