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Electrochemical impedance study on steel corrosion in the simulated concrete system with a novel self-healing microcapsule

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HIGHLIGHTS

- A microcapsule is designed for chemical self-healing target in concrete environment.
- An electrochemical model is proposed to state the property of microcapsule inhibitor.
- The microcapsule shows excellent protection against steel bar corrosion.

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ABSTRACT

Based on microcapsule technology, a new type of self-healing system for concrete materials was created, which mainly focuses on the corrosion protection of steel bars. In this paper, the performance of the system is characterized by means of the electrochemical impedance spectroscopy (EIS) of steel bar immersed in a simulated concrete environment. The experimental results demonstrate strong inhibition of chloride-induced corrosion when microcapsules are added to the water solution with sodium chloride by different mass fractions. A novel equivalent circuit model, which takes into account the inductive effect arising from the generation of corrosion products on the steel bar surface, is proposed to explain the protection performance of the microcapsules against the corrosion of a steel rebar in a concrete.

1. Introduction

Concrete is a primary material in modern construction. Because of creep, humidity changes and non-homogeneous settlement of buildings, concrete structures are highly susceptible to developing cracks during their service life. The cracks have a negative impact on safety, and may even cause serious accidents [1,2]. Self-healing technologies [3–5] can be used to repair the cracks in a concrete structure automatically, resulting in improved structural performance; such technology is being developed by incorporation of the new generation of smart structural materials [6–8].

Several methods have been developed for self-healing applications in concrete [9–11]. For example, incorporating AR-glass fibers can control the shrinkage cracks produced in young concrete. Another method involves the hydration of un-hydrated clinker available at the cracked surface, which can restore the continuity of the concrete. The recovery of the concrete structure is dependent on chemical reactions between the compounds within the concrete and the degree to which cracks can be filled with newly formed crystals.

Recently, a self-healing method based on hollow glass fibers/tubes containing adhesives has been investigated [5,8]. This technology does not require external monitoring because the cement matrix acts as a sensor. In this method, it is critical to control both the crack width and the size of the glass fibers used to achieve effective self-healing. An obvious limitation of using glass fiber capsules in concrete is their fragility, i.e. the brittle glass fibers would be easily broken during the stirring, vibration, curing and setting stages of a concrete. A related problem is that glass fibers carrying adhesive are difficult to distribute uniformly throughout the concrete matrix, as would be necessary in producing a self-healing concrete composite.

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The practical requirements of any self-healing concrete material include low cost, passive smartness and uniform distribution. The development of a smart concrete material should focus on engineering feasibility, high performance and small-volume applications for engineering practice [12–14]. One promising direction that satisfies these criteria is to incorporate microcapsules in a self-healing system, which was systematically established recently at Shenzhen University, China [15,16]. The proposed microcapsule-based self-healing system can be adopted not only for the performance healing concerning the crack repair and mechanical recovery, but also for the resistance recovery on the penetration of harmful ions (e.g. Cl^-, SO_4^{2-}, and CO_3^{2-}). Among various healing mechanisms, a novel chemical trigger mechanism in combination with a microcapsule-based corrosion inhibitor was introduced. Traditional, the corrosion inhibitors for steel bar reinforced concrete, such as $Ca(NO_2)_2$, Na_2PO_3F and so on, are mixed during the fabrication procedure, which makes a great waste of dosage. Whereas, the microcapsule packed with corrosion inhibitors can realize a controlled target for anti-corrosion of steel bar through the design both core and wall materials for microcapsule.

In this paper, the healing mechanism of the microcapsule for chloride-induced corrosion of steel bar in simulated concrete environment is studied. And, Polystyrene Resin (PS)/sodium monofluorophosphate (Na_2PO_3F) microcapsules were fabricated and characterized. The microcapsules were then put into a simulated concrete environment in order to evaluate the protection performance against steel corrosion by means of electrochemical impedance spectroscopy. A new electrochemical model was adopted to interpret the corrosion-inhibiting performance of the microcapsule system.

2. Experiments

The raw materials for preparation of the microcapsules are listed in Table 1. For microcapsule fabrication, sodium monofluorophosphate and polysorbate 80 were mixed into microcrystalline cellulose. The mixture was then formed into pellets with a cold extrusion rounded pelletizing machine, which uses high-speed centrifugation to round pellets into small spheres that act as microcapsule cores. The core was then placed into a spray coating machine, into which the capsule wall mixture made from talc powder, chloroform and polystyrene resin was injected. This mixture adheres to the surface of spherical cores to form the outer coating of the microcapsules. The resulting microcapsules were set via the spray drying method. The macro- and micro-morphology of microcapsule samples can be seen in Fig. 1.

To measure the steel corrosion in a microcapsule-based self-healing cementitious(simulated) system, a ∅10 (10 mm diameter) Q235 rebar was selected and rinsed with purified water, and successively cleaned by dilute hydrochloric acid and acetone. The rebar was then soaked for several hours in saturated calcium hydroxide solution to form a passivation film. Finally, one end of the bar was welded to a wire and daubed in epoxy resin to a depth of 7 cm. The working length is set as 5 cm to prepare for electrochemical impedance measurements.

In order to simulate a concrete environment, a saturated $Ca(OH)_2$ solution was prepared with a pH = 12.5. NaCl solution with varying concentrations was added in the $Ca(OH)_2$ solution to characterize the corrosion behavior of a steel rebar with varying microcapsule dosages. The amounts of NaCl and microcapsules used in each sample are listed in Table 2. The test with the electrochemical impedance spectroscopy was carried out by means of a Potentiostat/Galvanostat (Princeton Applied Research, Model 283). Saturated calomel electrode was used as the reference electrode. In order to observe the variation of steel corrosion with time, the tests were repeated at different exposure times.

The morphologicalchanges of the microcapsulesduring the steel corrosion process were observed by SEM (SU-70, Hitachi, Japan).

Table 1
Raw material for microcapsule fabrication.

Name	Product (source)
Sodium monofluorophosphate	Toothpaste-grade (XingFa Chemicals, Hubei)
Microcrystalline cellulose	Chemically pure (ShanHe Pharmaceuticals, Anhui)
Polysorbate 80	Chemically pure (YueQiao Reagent Plastics, Guangdong)
Talc powder	Chemically pure (XuFeng Powder, Quanzhou)
Polystyrene resin	Injection-molding grade (WanAn Biotechnology, Shanghai)
Chloroform	Analytical reagent (GuangHua Chemicals, Guangdong)

3. Results and analysis

For an ideal electrochemical system as illustrated in Fig. 2(a), two parallel processes exist: (1) charging/discharging of the electric double layer capacitor with varying potential across the electrodes (non-Faraday process); (2) Faraday's process (including charge transfer and diffusion) which occurs with a fixed potential across the electrodes [17,18]. The electrochemical system can thus be represented by the equivalent circuit model shown in Fig. 2(b).

Based on the above-mentioned schematic, the electrical circuit model for the idealized electrochemical system can be described by the CDC (Circuit Description Code) $R_s(Q(R_{ct}W))$ (see Fig. 2(b), $R_{ct} = Z_{ct}$, $W = Z_D$). Here, Q indicates C_d, the CPE (constant phase element) [19–21], which is generally attributed to distributed surface reactivity, surface inhomogeneity, roughness or fractal geometry, electrode porosity, and to current and potential distributions associated with electrode geometry. R_{ct} and W are the resistances associated respectively with charge transfer processes and diffusion processes. R_s represents the properties of the electrolyte solution and $(Q(R_{ct}W))$ reflects the reactions at the electrodes. The model can also be re-written as $R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2))$ (see Fig. 2(c)). $(Q_1(R_{ct1}W_1))$ and $(Q_2(R_{ct2}W_2))$ represent the functions of the left and right electrodes, respectively.

For steel corrosion in a microcapsule-based self-healing cementitious system, the process is more complex than that in an idealized electrochemical system as described above. With Cl^- attack, the steel rebar rusts and a layer of the corrosion product will deposit at the surface of the rebar, which results in an inductive effect during EIS measurement. In the microcapsule-based self-healing system, after the activation of the chemical trigger, the healing material inside microcapsule is in contact with the alkaline environment and the following chemical reaction will then take place:

$$6Ca^{2+} + 3PO_3^- + 3F^- + 6OH^- \rightarrow Ca_5(PO_4)_3F \downarrow + CaF_2 \downarrow + 3H_2O \quad (1)$$

The reaction products accumulate on the rebar surface, forming a protective layer against steel corrosion. Correspondingly, a new element must be added to the electrochemical model; the code $R_s((Q_1L_1)(R_{ct1}W_1))(Q_2(R_{ct2}W_2))$ can represent this system, as illustrated in Fig. 2(d). In this model, $((Q_1L_1)(R_{ct1}W_1))$ arises from the reaction at the surface of the rebar and $(Q_2(R_{ct2}W_2))$ from the reaction at the reference electrode. The total impedance of this model can be expressed as:

$$Z = Z_1 + Z_2 + Z_3 \quad (2)$$

where Z_1 is the impedance of rebar; Z_2 is the impedance of simulating concrete solution; Z_3 is the impedance of electrode.

Eq. (2) can be re-written as:

$$Z = \frac{(R_1+W_1)(1-\omega^2 Q_1 L_1)^2}{(1-\omega^2 Q_1 L_1)^2 + (R_1+W_1)^2} + R_s + \frac{1}{R_2+W_2} - \left\{ \frac{(R_1+W_1)^2(1-\omega^2 Q_1 L_1)}{(1-\omega^2 Q_1 L_1)^2 + (R_1+W_1)^2} Q_1 + \frac{(R_2+W_2)^2}{1+\omega^2 (R_2+W_2)^2 Q_2^2} Q_2 \right\} \omega j \quad (3)$$

where $L_1 = Z_L$, represents the inductance impedance; $\omega = 2\pi f$, represents the circular frequency

The real part of Z is:

$$Z' = \frac{(R_1+W_1)(1-\omega^2 Q_1 L_1)^2}{(1-\omega^2 Q_1 L_1)^2 + (R_1+W_1)^2} + R_s + \frac{1}{R_2+W_2} \quad (4)$$