A STUDY ON THE STEEL CORROSION PROTECTION OF A MICROCAPSULE BASED SELF-HEALING CEMENTITIOUS SYSTEM BY MEANS OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

Based on microcapsule technology, a new type of self-healing system for cementitious composites is established. The performance of the system was characterized by means of electrochemical impedance spectroscopy of steel bars immersed in a simulated concrete environment. The results demonstrate strong inhibition of chloride-induced corrosion when microcapsules are added to the solution. 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 steel bar corrosion in a concrete environment.

1. INTRODUCTION

Concrete is a basic material used for modern construction. Due to concrete creep, the humidity change and non-homogeneous settlement of buildings, concrete structures may generate a lot of cracks during service period. These cracks will affect the safety of the buildings and even cause severe accidents [1]. Self-healing technology then has been introduced to repair the cracks in a concrete structure automatically, resulting in an improvement of concrete structure performance [2-3]. An acceptable work that initiates an engineering approach for self-healing cement composite with microcapsules is first developed in Shenzhen University, China. Even so, existing efforts are focusing on the crack repair and mechanical performance recovery. It is not an effective method to deal with the degradation of the concrete structure, which caused by the ions erosion (such as Cl^-, SO_4^{2-}, CO_3^{2-} etc.). For this reason, a chemical trigger mechanism is proposed and a chemical self-healing system with microcapsule inhibitor is designed. And, its protection against steel corrosion is measured by means of electrochemical impedance spectroscopy [4]. A new electrochemical model is proposed to interpret the corrosion-inhibiting performance of the microcapsule system.

2. MATERIALS AND METHODS

For microcapsule fabrication, sodium monofluorophosphate and polysorbate 80 were mixed into sodium monofluorophosphate. And a spray drying method is used to form the microcapsule. With the aim of measuring steel corrosion within a microcapsule-based self-healing cementitious system, a Φ10 (10 mm diameter) Q235

rebar was prepared. In order to simulate a concrete environment, a saturated $Ca(OH)_2$ solution was prepared with pH=12.5. Different concentrations of $NaCl$ solution were added to the $Ca(OH)_2$ solution to characterize the corrosion behavior of the steel bar with varying microcapsule dosages. The amounts of $NaCl$ and microcapsules used in each sample are listed in Table 1. Electrochemical impedance spectroscopy of the steel bar corrosion was performed with a Potentiostat/Galvanostat (Princeton Applied Research, Model 283). A stainless steel 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.

Table 1: Concentrations of chloride ions and microcapsule dosage for each sample

Sample Number	A	B	C	D	E	F	G	H
chloride ion content (mg/L)	300	3000	6000	300	3000	6000	3000	3000
microcapsule content (g)	0	0	0	25	25	25	15	35

3. RESULTS AND DISCUSSION

For an ideal electrochemical system as illustrated in Figure 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. The electrochemical system can thus be represented by the equivalent circuit model shown in Figure 1(b). Based on the above 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 Figure 1(b), $R_{ct}=Z_{ct}$, $W=Z_D$). Here, Q indicates C_d, the CPE (constant phase element) [5], 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 $(Q_1(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ (see Figure 1(c)). $(Q_1(R_{ct1}W_1))$ and $(Q_2(R_{ct2}W_2))$ represent the functions of the left and right electrodes, respectively [6].

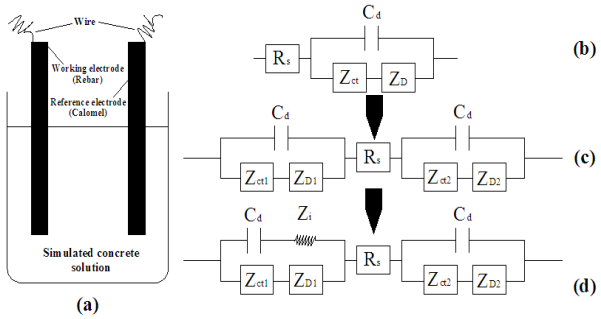

Figure 1: The electrochemical sketch map and equivalent circuit models.

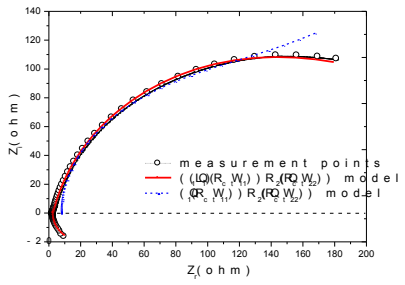

Figure 2: The Nyquist locus for steel corrosion within a microcapsule-based self-healing cementitious system under NaCl solution

In figure 1, R_s is resistance of electrolyte solution; C_d is electric double layer capacitance; Z_{ct} is resistance of charge transferring process and Z_D is resistance of diffusion process (Warburg resistance), where Z_{ct} and Z_D are composed as Z_F (Faraday's process).

For steel corrosion within a microcapsule-based self-healing cementitious system, the process is more complex than the idealized electrochemical system described above. With Cl^- attack, the steel bar rusts and a corrosion product layer will deposit at the surface of the rebar, which results in an inductive effect during EIS measurement. If microcapsules are added into the solution, they will break under the influence of 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 should 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 $((Q_1L_1)(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ can represent this system, as illustrated in Figure 1(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:

$$Z = \frac{(R_1+W_1)(1-\omega^2Q_1L_1)^2}{(1-\omega^2Q_1L_1)^2+(R_1+W_1)^2} + R_s + \frac{1}{R_2+W_2} - \{\frac{(R_1+W_1)^2(1-\omega^2Q_1L_1)}{(1-\omega^2Q_1L_1)^2+(R_1+W_1)^2}Q_1 + \frac{(R_2+W_2)^2}{1+\omega^2(R_2+W_2)^2Q_2^2}Q_2\}\omega j \quad (1)$$

Where, $L_1 = Z_i$, represents the inductance impedance; $\omega = 2\pi f$, represents the circular frequency [6]

Experimental measurements of the Nyquist for corrosion of the steel rebar within the microcapsule-based self-healing cementitious system in $NaCl$ solution are shown in Figure 2, along with fits from the equivalent-circuit models $((Q_1L_1)(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ and $(Q_1(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$. It is clear that the former model, which takes into account reactions at the rebar surface, gives a good fit both to the resistance and reactance loci depending to the frequency. Conversely, the $(Q_1(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ model gives a poor fit to the experiment results. In particular, the inductive effect arising from steel bar corrosion is manifested in the experimental data by values for the Nyquist locus for $Z'' \prec 0$ (i.e. in the fourth quadrant of Figure 2); this feature is not captured by $(Q_1(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$. The lack of agreement between $(Q_1(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ and the experimental results emphasizes that the model doesn't accurately represent the inductive effect caused by steel bar corrosion.

Figure 3 shows the Nyquist locus for steel corrosion with different Cl^- concentrations in a simulated concrete environment after a 100-day rusting period. It is clear that the Nyquist curves exhibit a similar trend regardless of the Cl^- concentration. All the loci have values in the fourth quadrant (i.e. $Z'' \prec 0$, $Z' \succ 0$) arising from the corrosion of the steel bar. Moreover, the locus shifts towards the left with increasing Cl^- concentration. In addition, Figures 3 show fits from the $((Q_1L_1)(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ model. The fitted values for the parameter L_1, which characterizes the inductive effect due to steel bar corrosion. It is found that L_1 increases with the length of the corrosion period and with increasing Cl^- concentration, which is consistent with the interpretation

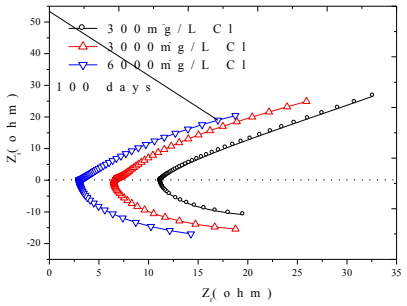

Figure 3: Nyquist locus and $((Q_1L_1)(R_1W_1))Rs((Q_2(R_2W_2))$ model fit for steel corrosion with different Cl^- concentrations in a simulated concrete environment

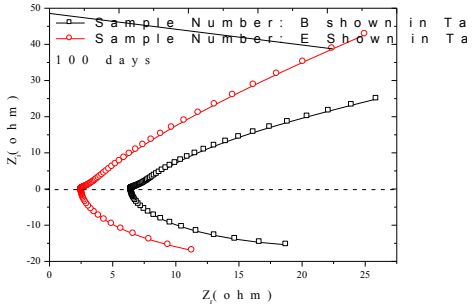

Figure 4: Comparison of Nyquist locus for steel bar corrosion with (E) and without (B) addition of microcapsules

of L_1 as arising from the generation of corrosion products on the surface of the steel bar. This gives support to the physical basis of the $((Q_1L_1)(R_{ct1}W_1))R_s(Q_2(R_{ct2}W_2))$ model and its corresponding parameter L_1, as an accurate description of the experimental situation. Microcapsules were added to a number of the simulated concrete-rebar systems, and the resulting samples compared with the corresponding no-microcapsule samples to assess the extent to which the microcapsules could protect against corrosion (shown in Figure 4). Regardless of the addition of microcapsules, the electrical inductance feature (Nyquist loci present for $Z_i < 0$) is observed. However, the difference in the L_1 value between the two cases is dramatic: L_1 for that with microcapsule sample (E) is smaller than that for the no-microcapsule sample (B) by roughly four orders of magnitude after 100 days. Since L_1 relates to the amount of corrosion products generated, this clearly demonstrates a strong protective effect of the microcapsules against corrosion of the steel bar by Cl^- ions.

4. CONCLUSION

A new kind of microcapsule has been designed, and its anti-corrosion characteristics is studied in the context of steel bar corrosion triggered by Cl^- ions in a simulated concrete environment with a new electrochemical model, which takes into account the inductive effect caused by the rust layer at the surface of the steel bar. The parameter L_1 in the model is obtained by fitting to experimental data and thus its dependence on the corrosion period, Cl^- concentration are determined. The microcapsule approach is capable of providing excellent protection against steel bar corrosion.

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