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Study of steel corrosion in strain-hardening cementitious composites (SHCC) via electrochemical techniques

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Abstract

This paper investigates corrosion of steel bar in reinforced strain-hardening cementitious composites (R/SHCC) through electrochemical techniques. Linear polarization resistance is engaged to determine corrosion rate of steel bar while electrochemical impedance spectroscopy is employed to study corrosion kinetics by probing the electrode and interface reactions. An equivalent circuit model is used to quantitatively interpret the impedance data of steel corrosion. Results show that polarization resistance R_p of R/SHCC is much higher than that of R/M and thus corrosion rate of steel bar in R/SHCC is much reduced. The R_p of R/SHCC is about two orders of magnitude higher while the corrosion rate of R/SHCC can be two orders of magnitude lower than that of R/M after 137 h accelerated corrosion. R_p of specimen is dominated by the charge transfer resistance R_{ct} before cover cracking and governed by both R_{ct} and cover resistance R_c after cover cracking. R/SHCC specimen possesses a much higher R_{ct} and R_c than R/M due to high tensile ductility and damage tolerance of SHCC material together with tight crack with in SHCC cover.

Keywords: corrosion kinetics; strain-hardening cementitious composites; linear polarization resistance; electrochemical impedance spectroscopy; equivalent circuit

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List of Symbols and Abbreviations

C_C	Cover capacitance
ε_{ut}	Tensile strain capacity
f'_c	Compressive strength
n	CPE power index
Q_{dl}	Constant phase element (imperfect capacitance)
R_c	Cover resistance
R_{ct}	Constant phase element (charge transfer resistance)
R_p	Polarization resistance
R_s	Solution resistance
σ_{ut}	Tensile strength
ω	Frequency
Y_0	Admittance
Z_{CPE}	Impedance of constant phase element
CPE	Constant phase element
CR	Corrosion rate
DC	Direct current
EIS	Electrochemical impedance spectroscopy
LPR	Linear polarization resistance
LVTD	Linear variable displacement transducer
OPC	Ordinary Portland cement
PVA	Polyvinyl alcohol
R/C	Reinforced concrete
R/M	Reinforced mortar

R/SHCC	Reinforced strain hardening cementitious composite
SCE	Saturated calomel electrode
SE	Secondary electron
SHCC	Strain hardening cementitious composite
SP	Superplasticizer

1 Introduction

Corrosion of steel reinforcement is the major durability concern of reinforced concrete (R/C) structure because it reduces the cross sectional area of rebar, compromises the bond between rebar and concrete, and causes cracking, delamination and spalling of concrete cover. Due to the high alkaline environment in concrete (pH ~12-13), steel reinforcement in concrete is inherently protected by a thin passivation layer mainly composed of iron oxide constituent Fe_2O_3 in very condense form [1]. Carbonation of concrete and ingress of acidic chemicals such as SO_2 from environment, however, can reduce the alkalinity of concrete and cause depassivation of steel [2-4]. Besides, infiltration of chloride ion from deicing salt, seawater and other sources through concrete cover can also severely destroy the passivation layer. All these lead to corrosion of steel reinforcement [1, 5]. Corrosion of steel can be divided into two half-cell reactions, i.e. anode reaction and cathode reaction. Anode reaction produces ferrous ions and cathode reaction produces hydroxyl ions. Ferrous ions combine with the hydroxyl ions to form ferric hydroxide, which is further oxidized to rust with the presence of oxygen.

Strain hardening cementitious composite (SHCC) is a unique class of high performance fiber-reinforced concrete possessing tensile strain hardening behavior with extreme tensile ductility several hundred times that of conventional concrete and self-controlled tight crack width

below 100 μm even at ultimate strain capacity [6]. Studies showed that SHCC cover significantly slows down corrosion of steel reinforcement in comparison with normal concrete [7-10]. Specifically, corrosion-induced mass loss rate of steel bar in reinforced SHCC (R/SHCC) specimens was found to be one order smaller than that in the reference reinforced mortar (R/M) specimens [11, 12]. This was thought to be attributed to the high ductility and damage tolerance of SHCC cover and tight crack width in SHCC material, which may restrain the ingress of harmful substances and reduce the egress of rust and then slow down corrosion [13-16].

Electrochemical tests are useful techniques to obtain information of corrosion. Among different electrochemical measurements, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) are often used. LPR provides real time monitoring of corrosion rate because polarization resistance R_p can be related to corrosion current by the Stern-Geary equation [17, 18], where R_p is inversely proportional to corrosion current. EIS is often engaged to investigate corrosion kinetics of coated metal [19, 20] and steel reinforcement in R/C [21, 22]. An important advantage of EIS in comparison with other techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. EIS is capable of characterizing bulk and interfacial properties of the system across a wide range of frequency. Depending upon the shape of the EIS spectrum, equivalent circuit models and initial circuit parameters are assumed to quantitatively interpret the impedance data of steel corrosion. Pech-Canul and Castro [23] proposed one-loop Randles circuit modified by replacing capacitor with constant phase element (CPE) and adding Warburg element in series combination with charge transfer resistor so as to approximate the electrochemical impedance of steel in concrete in tropical marine atmosphere. Choi et al [21] used modified one-loop circuit to model the passive steel

in the concrete and proposed series-connected two-loop circuit to simulate pitting corrosion of steel in concrete. Qiao and Ou [24] simulated the corrosion behavior of carbon steel in cement mortar without coarse aggregates. Specifically, the mortar cover was modelled as capacitor, the interface between rebar and cover was modeled as CPE, and Warburg element connected with charge transfer resistor in series was used to capture diffusion effect.

While studies showed that SHCC cover significantly slows down corrosion of steel reinforcement in comparison with normal concrete [7-16]. Fundamental mechanisms of steel corrosion in R/SHCC such as corrosion kinetics and electrode and interface reactions have yet been investigated by means of electrochemical techniques. Furthermore, no equivalent circuit model and initial circuit parameters have been proposed to quantitatively interpret the impedance data of steel corrosion in SHCC. In this study, the electrochemical techniques including LPR and EIS were used for the first time to investigate corrosion of steel reinforcement in R/SHCC. LPR was engaged to determine corrosion rate of steel reinforcement and EIS was employed to study corrosion kinetics by probing the electrode and interface reactions. An equivalent circuit model for corrosion of steel reinforcement in R/SHCC was proposed and the model was used to quantitatively interpret the impedance data to reveal the underlying mechanisms of steel corrosion in R/SHCC.

2 Experimental programs

2.1 Raw materials and mix proportion of cover materials

Raw materials used for the preparation of SHCC and reference mortar include ordinary Portland cement, class F fly ash, silica sand, PVA fiber, water and superplasticizer. The average particle size of silica sand is 110 micrometers. The PVA fibers (39 μm in diameter and 12 mm in length) used has a nominal modulus of 41 GPa and a tensile strength of 1600

MPa. The mix proportions by weight ratio of SHCC and the reference mortar are shown in table 1. The reference mortar consists of 30% OPC and 70% fly ash by weight with water-to-binder ratio of 0.27 and sand-to-binder ratio of 0.36. 2% of PVA fiber by volume was added into the same binder matrix for the preparation of the SHCC mix.

2.2 Specimen preparation

To prepare the reinforced SHCC (R/SHCC) and reinforced mortar (R/M) specimens, plain steel bars (structural carbon steel, grade SS 41, $\phi = 13$ mm) without ribs were used in this study and the composition is shown in table 2. The surface of the steel bars was polished by using a lathe and sand papers to remove the mill scale and oil. The top and bottom ends of the steel bar were coated with epoxy to prevent the ends from corrosion, leaving a free length of 100 mm in the middle portion (i.e., area of working electrode of 40.82 cm^2) exposed to the environment for active corrosion. The dimension and details of the lollipop specimen are schematically shown in Fig. 1. The steel bar was placed in the center of the cylindrical specimen ($\phi = 75$ mm and $L = 200$ mm) and extruded from the top surface (25 mm) to form a lollipop specimen. To prepare fresh SHCC mix, all solid ingredients (except fibers) were dry-mixed in a planetary mixer for two minutes followed by the addition of water and superplasticizer. When the fresh paste was consistent and homogenous, PVA fibers were then slowly added to the mixture and mixed for another three minutes to achieve good fiber dispersion. The fresh mixture was poured into the molds and consolidated using a vibration rod to remove the entrapped air. Four lollipop specimens were prepared for each mix. At the same time, the 50 mm cubic specimens and dog-bone specimens were also prepared to determine the mechanical properties of cover materials. After casting, the open top surface was sealed with plastics to prevent water evaporation, and the specimens were placed in the laboratory air condition (23°C and 65% RH) for one day. After which, the specimens were

demolded and cured in a sealed plastic container (23°C and 90% RH) for other 27 days before the mechanical properties and corrosion test.

2.3 Test methods

2.3.1 Mechanical properties

The compressive strength of SHCC and mortar was determined using 50 mm cube according to BS EN 12390-3:2009. The loading rate of compressive strength test was 100 kN/min. The compressive strength was recorded as an average of three cubes.

The tensile behavior of SHCC and mortar was determined using the dog-bone specimen. A displacement-controlled uniaxial tensile test was conducted on dog-bone specimen using an electronic universal testing machine with 50 kN capacity. Two LVTD were used to monitor the deformation of the specimen with a gage length of 100mm. The test was carried out under displacement control at a rate of 0.2 mm/min. Four dog-bone specimens were prepared for obtaining the average result.

2.3.2 Accelerated corrosion test

Accelerated corrosion, similar to those used in other studies [25-28], was adopted in the current investigation. Fig. 1b schematically shows the accelerated corrosion experiment apparatus. The lollipop specimen was kept in 3.5 wt.% sodium chloride solution. A DC power supply (Keysight N6701A low-profile modular power system with four slots) was used to impose a constant potential of 15V on the steel bar which served as a working electrode and attached to the positive output terminal of the DC power supply, whereas the steel mesh (sourced from MIKAS Stainless Steels Pte Ltd, and table 2 shows its composition) near the specimen served as an auxiliary electrode and connected to the negative output

terminal. The relatively higher voltage was used to accelerate the corrosion process in a shorter period. After every 24-hour accelerated corrosion (blue bar), the specimen rest for another 24 hours without going through any accelerated corrosion (red line) as shown in Fig. 2. The free standing period was to allow the corrosion process to achieve a steady state. LPR and EIS measurements were conducted at the end of each cycle (green circle). After the measurement, another cycle of accelerated corrosion/resting was carried out.

2.3.3 Electrochemical test

A three-electrode measurement system was used to measure the electrochemical response. The steel bar, the stainless steel wire mesh, and the saturated calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively. LPR and EIS measurements were carried out by means of a potentiostat (VersaSTAT4, Princeton Applied Research). In EIS measurement, the magnitude of the ac potential signal was 10 mV and the frequency range was 0.01 Hz to 100000 Hz with 10 measurements per decade. In LPR measurement, the specimen was polarized from initial potential of $E_{oc}-10$ mV to the final potential of $E_{oc}+10$ mV with a scan rate of 0.125 mV/s.

2.3.4 Microstructure analysis

A thin slice sample was cut by Buehler ISOMET 2000 diamond saw from R/SHCC for SEM characterization and EDX microanalysis. Before microstructure analysis, the sliced samples were first impregnated with epoxy, followed by grinding and finely polishing with different grits of sandpapers and ethanol to reveal the fresh rust layer. Field emission SEM equipped with EDX (JEOL JSM-7600) was used to characterize the microstructure and element mapping of the rust layer in the sliced samples. A gentle beam mode (GB mode) with a low accelerating voltage of 2 kV and probe current of 5 A was used in the FESEM study to obtain

high-resolution secondary electron images. A high accelerating voltage of 15kV and probe current of 9 A were used to obtain the element mapping.

3. Results and discussion

3.1 Mechanical properties of cover materials

The mechanical properties of the SHCC and the reference mortar are summarized in table 1. As can be seen, SHCC and reference mortar have comparable 28-day compressive strength of around 40 MPa owing to both mixes have the same water-to-binder ratio. Figure 3 shows the typical tensile stress-strain curves of SHCC and the reference mortar. As can be seen, the tensile strength of SHCC is 4.6 ± 1.2 MPa while that of the reference mortar is 3.1 ± 0.8 MPa. SHCC exhibits tensile strain hardening behavior with a tensile strain capacity of 3.3 ± 1.2 % while mortar shows post-cracking brittle failure.

3.2 Polarization resistance and corrosion rate

Fig. 4 plots polarization resistance R_p and corrosion rate as functions of corrosion duration. Corrosion rate (CR) is expressed as corrosion current density in $\mu\text{A}/\text{cm}^2$. The general trend shows that R_p decreases while the corrosion rate increases with increasing duration of corrosion. The R_p values for the pristine samples (both R/M and R/SHCC) can achieve more than $2000 \text{ k}\Omega \cdot \text{cm}^2$, which is in the same order of magnitude as compared to other studies [29, 30]. The R_p of R/M decreases dramatically with increasing corrosion duration. After cover cracking of R/M, the R_p is more than one order of magnitude lower than the pristine sample, which is consistent with published results [30]. As can be seen, R/SHCC possesses a higher R_p than R/M at any given duration of corrosion. Ratio of $R_{p,R/SHCC}$ to $R_{p,R/M}$ increases with increasing corrosion duration (Fig. 5). The R_p of R/SHCC is about two orders of magnitude higher than that of R/M after 137 h accelerated corrosion. Furthermore, the R/SHCC has a

significantly lower corrosion rate in comparison with the R/M (Fig. 5). The R/SHCC sample maintains a low and steady corrosion rate even after 209 h of accelerated corrosion, while the R/M sample shows a significant increase of corrosion rate after 89 h accelerated corrosion. Ratio of $CR_{R/SHCC}$ to $CR_{R/M}$ decreases with increasing corrosion duration (Fig. 5). The corrosion rate of R/SHCC can be two orders of magnitude lower than that of R/M after 137 h accelerated corrosion.

This is mainly attributed to the extreme tensile ductility and high damage tolerance of SHCC material which significantly delays crack initiation and slows crack propagation in cover of R/SHCC subject to expansion of corroded steel reinforcement during accelerated corrosion [31, 32]. It is observed that cracks propagated throughout the cover of R/M after 89 h accelerated corrosion. Cracks on cover of R/M widen quickly with prolonged corrosion due to the brittle nature of mortar. Formation of wide open cracks provides pathways for the easy ingress of chloride ions to reach the surface of steel bar, which further accelerated the corrosion process [33]. On the contrary, cover cracks of R/SHCC specimen are observed only after 209 h accelerated corrosion. Instead of widening of crack opening, many microcracks with tight crack width below 0.1 mm are found on the cover of R/SHCC after prolonged corrosion. Formation of tight microcracks hinders the migration of rust, resulting in accumulation of corrosion products inside the microcracks (Fig. 6) and filling of the pathway which not only prevents the egress of rust but also reduces the ingress of chemicals. Therefore, corrosion rate of R/SHCC is much reduced even after cover cracking.

3.3 Electrochemical impedance spectroscopy

Figure 7 shows the Nyquist plots of R/M and R/SHCC after different duration of accelerated corrosion. As can be seen, two incomplete capacitive arcs are observed in the Nyquist plots.

One is at the low frequency region (arc on the right from 0.01 Hz to 100 Hz) governed by charge transfer resistance from the steel bar and diffusion of chemical species while the other is at the high frequency region (arc on the left from 100 Hz to 100000 Hz) dominated by the bulk matrix and pore structure of cover material [34]. Before corrosion, the slope of low frequency capacitive arc of R/M is high and is similar to that of R/SHCC indicating good and comparable steel/matrix interface characteristics for both covers. The slope of low frequency capacitive arc reduces with increasing corrosion duration, which implies deterioration of interface between the steel bar and the surrounding matrix [34]. The low frequency capacitive arc shrinks into a short flat line after cover cracking, which indicates the interface becomes insignificant in affecting the impedance response. The deterioration rate of interface in R/SHCC, however, is much gentle as compared to that in R/M. This may be attributed to the formation of multiple cracks in SHCC cover with tight crack width resulting in microcell corrosion, which greatly reduces corrosion and interface deterioration rates [35].

Intersection of the left capacitive arc (high frequency range) with the x-axis denotes the real part of the impedance of the system, which can be approximately considered equal to the resistance of the cover system [36]. As can be seen from the expanded region at the lower values of real impedance in Fig. 7 (inset), the resistance of SHCC cover (Fig. 7b, inset) at the pristine stage before corrosion is higher than that of mortar cover (Fig. 7a, inset), which may be due to the reduction of shrinkage-induced cracking in SHCC cover because of the addition of PVA fibers [37]. Resistance of cover material increases slightly with increasing corrosion duration before cover cracking at 89 and 209 hours for R/M and R/SHCC, respectively. This may be attributed to the continued and accelerated hydration of the cover material in NaCl solution resulting in reduction of porosity and thus increasing resistance [38-40]. Upon cover cracking; however, resistance of cover material reduces significantly because the open crack

permits the penetration of solution and the current can easily pass the cover material through the solution in the cracks and thus the resistance of system reduces significantly.

Figure 8 displays the Bode plots of the R/M and R/SHCC specimens after different duration of accelerated corrosion. A partial peak can be observed in the phase angle plots at low frequency range indicating capacitive behavior at low frequency domain. This peak decreases with increasing corrosion duration and disappears after cover cracking. It is plausible that the capacitive behavior at low frequency domain is not only related to the passive state of surface of steel bar but also dominated by the integrity of cover material. The reduction rate of phase angle of R/SHCC is much slower than that of R/M which is attributed to strong cracking resistance of the SHCC cover. The impedance $|Z|$ at the low frequency range also decreases with increasing corrosion duration. The decrease of impedance indicates the decay of capacitive behavior which can be attributed to the destruction of interface between cover and steel bar due to the presence and accumulation of corrosion products. R/SHCC again shows a gentle decrease of impedance when compared with R/M, which suggests SHCC cover possesses better property to sustain the capacitive behavior. This is mainly attributed to the high ductility and damage tolerance of SHCC which provides strong confinement to the corroded steel.

3.4 Equivalent circuit

Corrosion consists of many simultaneous electrochemical and physical processes. Different electrical component was used to represent the impedance response of steel bar, concrete matrix and the interface. Several equivalent circuits were proposed to capture the EIS response of R/C [24, 41-43]. For R/C system in sodium chloride solution, at least three interfaces i.e. interface of electrolyte and bulk matrix, the inner bulk matrix, and the

steel/matrix interface, should be considered [44]. Figure 9 shows the equivalent circuit used in the current study, which is composed of two time constants in series and the electrolyte resistance and the diffusion effect were also taken into account.

The element R_s represents the ionic conduction of the solution. The first time constant (R_c and C_c) is related to the properties of cover in terms of bulk matrix and pore structures. The second time constant (R_{ct} and Q_{dl}) is attributed to the electrochemical reaction on the interface between steel and cover. The charge transfer resistance R_{ct} represents the process of transferring charge species or electric ion from electrode to electrolyte. Element Q_{dl} represents the double layer behavior of interface between the steel bar and cover. In the equivalent circuit model, constant phase element (CPE) is used instead of pure capacitor to account for the imperfect capacitive behavior. It could be attributed from surface roughness, interfacial phenomena [45]. The impedance of CPE could be represented as Eqn. 1.

$$Z_{CPE} = -\frac{1}{(j\omega)^n Y_0} \quad (1)$$

where, Z is the impedance, ω is frequency, Y_0 is admittance, and n is the CPE power index. CPE represents a capacitor and a resistor when n equals 1 and zero, respectively.

An iteration process was carried out to determine the value of each electrical component in the proposed equivalent circuit so that the modeled EIS results can best fit the experimental EIS results. Figure 10 compares the measured and simulated impedance spectra of both R/M and R/SHCC samples. As can be seen, the simulated results fit well with the measured data at different stages (i.e., pristine, before cover cracking and after cover cracking), which suggests the proposed equivalent circuit may able to describe corrosion kinetics and capture electrode and interface reactions of both R/M and R/SHCC samples. Table 3 summarizes derived values of electrical components in the proposed equivalent circuit of R/SHCC and R/M after

different duration of accelerated corrosion. As can be seen, electrical resistance of electrolyte R_s is very small and does not contribute significantly to the impedance of the system. Cover electrical resistance R_c of SHCC before corrosion is more than three times that of mortar possibly due to the inclusion of PVA fiber in SHCC which reduces shrinkage cracking in the SHCC cover [39]. Furthermore, R_c of both SHCC and mortar covers increases moderately with increasing corrosion duration before cover cracking (Fig. 11a), which may be attributed to the continued and accelerated hydration of the cover material in the presence of chloride ions resulting in reduction of percentage of connective pores and thus increasing resistance of cover materials [46]. Upon cover cracking; however, R_c reduces drastically (Fig. 11a) because the open crack permits the penetration of solution and the current can easily pass the cover material though the solution in the cracks and thus the resistance of system reduces significantly. It should be noted that SHCC cover (even after cracking) possesses higher electrical resistance than the mortar cover at all stages. This is attributed to the high ductility and damage tolerance of SHCC material which prevents destructive failure and maintains integrity of cover. The tight crack width in SHCC cover may hinder the migration of rust, resulting in accumulation of corrosion products inside the microcracks and filling of the pathway (Fig. 6). Both contribute to high electrical resistance of SHCC cover even after cracking.

Charge transfer resistance R_{ct} is a direct indication of the easiness of transporting electrons from the steel bar to the surrounding solution/matrix and reacting with oxygen [47]. As can be seen, a drastic reduction of R_{ct} from the order of 10^5 ohms to the order of 10^4 ohms for both R/SHCC and R/M specimens after only one cycle of accelerated corrosion (Fig. 11b). This is attributed to depassivation of steel in both R/SHCC and R/M specimens subject to accelerated corrosion. After depassivation of steel reinforcement, R_{ct} reduces moderately with

increasing corrosion duration. R_{ct} of R/SHCC; however, is significantly higher than that of R/M at any given corrosion duration. This may be attributed to the strong confinement of SHCC cover to the corroded steel resulting in the formation of a dense rust layer (Fig. 12), which hinders free ions movement. This finding is consistent with the research of Šavija et al [13, 48]

Polarization resistance R_p of specimen can be roughly determined from the summation of electrolyte resistance R_s , cover resistance R_c , and charge transfer resistance R_{ct} [36]. As can be seen from table 3, R_{ct} in both R/SHCC and R/C is several orders higher than R_s and R_c before cover cracking and thus dominates R_p of specimen. After cover cracking, both R_{ct} and R_c govern R_p of specimen. It is observed that SHCC cover possesses overall high R_p (and thus enhanced corrosion resistance) than mortar cover as shown in Fig. 11c, which is in agreement with the LPR results.

4 Conclusions

Corrosion of steel bar in R/SHCC and R/M were investigated by means of electrochemical techniques including LPR and EIS. LPR was engaged to determine corrosion rate of steel bar and EIS was employed to study corrosion kinetics by probing the electrode and interface reactions. An equivalent circuit model for corrosion of steel bar in R/SHCC was proposed and the model was used to quantitatively interpret the impedance data of steel corrosion. Results show that polarization resistance R_p of R/SHCC is much higher than that of R/M and thus corrosion rate of steel bar in R/SHCC is much reduced. **The R_p of R/SHCC is about two orders of magnitude higher while the corrosion rate of R/SHCC can be two orders of magnitude lower than that of R/M after 137 h accelerated corrosion.** R_p of specimen is dominated by the charge transfer resistance R_{ct} before cover cracking and governed by both R_{ct} and cover resistance R_c after cover cracking. R/SHCC specimen possesses a much higher

R_{ct} and R_c than R/M due to high tensile ductility and damage tolerance of SHCC material together with tight crack with in SHCC cover.

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Table 1 Mix proportion of SHCC and reference mortar

Specimen	Cement	Fly ash	Sand	Water	SP ^a	PVA ^b	f_c (MPa)	σ_{ut} (MPa)	ε_{ut} (%)
SHCC	1	2.33	1.20	0.90	0.01	0.07	46±3.6	4.6±1.2	3.3±1.2
mortar	1	2.33	1.20	0.90	0.01	0.00	43±2.1	3.1±0.8	-

Note: ^a SP-Superplasticizer; ^b PVA-polyvinyl alcohol fiber; f_c : compressive strength; σ_{ut} : tensile strength; ε_{ut} : tensile strain capacity

Table 2 Chemical compositions of steel bar and stainless steel wire mesh

	C	Mn	S	P	Si	Ni	Cr	Mo	N
Steel bar	0.14-0.2	0.36-0.65	≤0.05	≤0.045	≤0.30	-	-	-	-
Steel mesh	0.021	1.72	0.004	0.04	0.26	10.08	16.65	2.03	0.06

Table 3 Derived value of each electrical component of the proposed equivalent circuit of

R/SHCC and R/M after different duration of accelerated corrosion

Duration (hours)	R_s ($\Omega \cdot \text{cm}^2$)	C_c ($\mu\text{F}/\text{cm}^2 \cdot 10^{-3}$)	R_c^* ($\text{k}\Omega \cdot \text{cm}^2$)	Q_{dl-Y_0} ($\text{ohm}^{-1} \cdot \text{s}^n/\text{cm}^2$)	Q_{dl-n}	R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)
R/SHCC						
0	8.45E-04	0.018	29.0	2.65E-05	0.876	15674.9
41	2.74E-03	0.018	32.4	2.96E-05	0.902	2526.8
89	9.55E-04	0.018	34.2	9.51E-05	0.839	2200.2
137	1.66E-03	0.017	32.9	1.05E-04	0.772	600.1
185	2.39E-03	0.017	35.2	1.50E-04	0.732	256.3
209	1.38E-03	0.018	33.2	2.13E-04	0.328	71.8
233	1.33E-03	0.022	21.5	2.30E-04	0.132	13.7
257	1.25E-03	0.029	15.1	3.11E-04	0.110	10.5
R/M						
0	6.04E-03	0.038	8.1	3.53E-05	0.901	21389.7
17	5.39E-03	0.034	9.9	3.45E-05	0.899	849.1
41	1.03E-03	0.031	11.1	3.67E-05	0.887	636.8
89	5.80E-04	0.026	13.6	1.30E-04	0.795	70.2
113	1.90E-04	0.032	9.6	6.88E-04	0.121	42.0
137	5.35E-05	0.048	5.5	1.58E-03	0.106	34.9

Note: * Data are normalized by area of electrode, and the area of electrode is 40.82 cm^2 .

Fig. 1 Configuration of the lollipop specimen for corrosion test and schematic representation of the accelerated corrosion apparatus (unit: mm). (a) Top view of the lollipop specimen:

The steel bar is located at the center of the specimen with both ends of the steel bar are coated with epoxy and protected by heat shrinking tube; the screw hole at the top of the steel bar is used to connect the steel bar to the DC power supply through a cable. (b) Configuration of the accelerated corrosion test: The specimen is immersed in 3.5% NaCl solution, and the solution

level is 20 mm below the top surface of the specimen; the steel bar and stainless steel wire mesh are connected to the positive and negative polarities of the DC power supply, respectively, with an applied potential of 15 V.

Fig. 2 Cyclic accelerated corrosion regime. Each cycle consists of a 24 h accelerated corrosion period (15 V) followed by a 24 h free standing period (0 V).

Fig. 3 Uniaxial tensile stress-strain curve and crack pattern of mortar and SHCC. The mortar shows a brittle failure mode with single crack, while the SHCC exhibits a tensile strain-hardening behavior with multiple micro cracks.

Fig. 4 (a) Polarization resistance of R/M and R/SHCC determined by the LPR test, and (b) corrosion rate of steel bar determined by the Faraday's law as a function of corrosion duration. Markers are the measured data and dashed lines are fitted results by means of regression

Fig. 5 Ratio of $R_{p, R/SHCC}$ and $R_{p, R/M}$ and ratio of $CR_{R/SHCC}$ and $CR_{R/M}$ as a function of corrosion duration.

Fig. 6 Corrosion-induced cover cracking and migration of corrosion products in R/SHCC: (a) Overview of multiple microcracks formed around steel bar in the cross-section of R/SHCC specimen; (b) SE image at steel and cover interface showing rust layer and microcracks; (c) EDS mapping of Fe element showing the rust layer and the microcracks filled with rust; (d) EDS mapping of Si element showing the SHCC cover layer with micro cracks.

Fig. 7 Nyquist plots of (a) R/M and (b) R/SHCC after different duration of accelerated corrosion (frequency range: 100 kHz to 10 mHz). The insets are expanded region at the lower values of real impedance.

Fig. 8 Bode plots of (a) R/M and (b) R/SHCC after different duration of accelerated corrosion (frequency range: 100 kHz to 10 mHz).

Fig. 9 Equivalent circuit used to model the experimental EIS data with two time constants.

The first time constant (R_c and C_c) is related to the properties of cover in terms of bulk matrix and pore structures. The second time constant (R_{ct} and Q_{dl}) is attributed to the electrochemical reaction on the interface between steel and cover.

Fig. 10 Comparison between measured and simulated impedance spectra at different stages (i.e., pristine, before cover cracking and after cover cracking). (a) R/M, Nyquist plot; (b) R/SHCC, Nyquist plot; (c) R/M, Bode plot; and (d) R/SHCC, Bode plot.

Fig. 11 Evolution of resistances as a function of corrosion duration obtained from equivalent circuit fitting: (a) Cover resistance, R_c ; (b) charge transfer resistance at interface, R_{ct} ; and (c) polarization resistance of system, R_p .

Fig. 12 Microstructure of rust layer: (a) Overview of multiple microcracks formed around steel bar and the rust layer profile in the cross-section of R/SHCC specimen; (b) SE image of rust layer at the position of thin rust layer; (c) SE image of dense rust layer in the vicinity of crack, a small gap was observed between the rust layer and the SHCC cover; (d) SE image of rust layer at the position of thick rust layer.

- LPR and EIS are used to investigate steel corrosion of R/SHCC
- An equivalent circuit is proposed to model EIS response of R/SHCC
- R/SHCC possesses a much higher corrosion resistance, R_{ct} and R_c , than R/M
- R_p is dominated by R_{ct} before cover cracking and governed by both R_{ct} and R_c after cover cracking