Effect of Endogenous Chloride Ion on Corrosion of Rebar in Sea-sand Ultra-high Performance Concrete

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Abstract. *Ultra-high performance concrete (UHPC) is an innovative cement-based composite material characterized by extremely high durability and mechanical properties, which provides a potential possibility of using non-desalted sea-sand as aggregate. However, the long-term steel corrosion behavior in UHPC prepared by simulated sea-sand under different immersion environments remains unclear. In this study, the pore structure of sea-sand UHPC matrix was measured using nitrogen adsorption/desorption method. The corrosion behavior of rebar in sea-sand UHPC with different endogenous chloride ion contents soaking in pure water and NaCl solution was characterized by electrochemical workstation. The experimental results show that the initial UHPC pore structure is refined by incorporation ofsea-sand, and is similar to that of ordinary UHPC at the later hydration. Regardless of the endogenous chloride ion content and immersion environment, the corrosion rate evaluated by corrosion current density (icorr) and polarization resistance (Rp) of reinforcement in UHPC is extremely low. The measurement of EIS shows that UHPC group has higher matrix resistance (Rc) and charge transfer resistance (Rct), while lower electric double layer capacitance (CPEdl) of reinforcement, which indicates that the steel in UHPC made of sea-sand is still in a state ofpassivation. However, the steel bar in comparison specimen OPC soaking in NaCl solution is in the corrosion stage. Furthermore, sea-sand UHPC possesses of excellent ability of anti-pitting corrosion ofreinforcement after 180 days ofimmersion in NaCl solution.*

Keywords: *Sea-sand UHPC，Pore structure, Corrosion behavior, Endogenous chloride level, Immersion environment.*

1 Introduction

River sand resources are scarce, while sea sand resources are abundant. However, mass of chloride ions carried in sea-sand would cause the corrosion of reinforcement embedded in concrete. traditional desalination methods commonly consume large amounts of freshwater and electricity, therefore, it is a great necessity to explore the application of non-desalinated sea-sand in concrete. Ultra-high performance concrete (UHPC) is an innovative cementitious engineering material, which provides us potential possibility of using non-desalted sea-sand as aggregate without causing corrosion of reinforcement. To

obtain a better understanding of the engineering application of sea sand UHPC, many researchers have exploited the chloride ion in sea sand UHPC. Wei found that the cement hydration of UHPC was promoted by the endogenous chloride ion released from the sea-sand. Using of sea-sand could refine the pore structure in the early age, but insignificant difference in the total porosity was found between sea-sand UHPC and traditional UHPC at the later age. Chen and Ni revealed that the chloride ion permeability of in sea-sand UHPC could be ignored regardless of endogenous chloride ion level, and the reinforcement protection ability of sea-sand UHPC was much higher than that of common sea-sand concrete.

Such research outcomes are necessary, but the influence on the long-term reinforcement corrosion behavior in sea-sand UHPC with different chloride ion content remains unclear. In this study, a series of experiments are devised to study the effect of chloride ion introduced by simulated sea-sand on the reinforcement long-term corrosion behavior in different immersion environment.

2 Materials and Methods

2.1 Materials

The UHPC mixture formulations are presented in Table 1. The diameter and length of rebar are 6 mm and 150 mm, respectively. Deionized water is used in this study.

The investigated simulated sea-sand codified as S1, S3, S5 and S7, was obtained by immersing the quartz sand into 1%, 3%, 5% and 7% of NaCl solution, respectively. The measurement result of chloride ion content attached by simulated sea-sand which was in accordance with Chinese Code (JGJ52-2006) is shown in Table 2. The corresponding sea-sand UHPC mixes are denominated as U-S1, U-S3, U-S5 and U-S7, respectively. Meanwhile, a reference mix noted as OPC were prepared for the comparison.

Table 1. Formulations of specimens / $(kg \cdot m^{-3})$.

	Cement	Silica fume	Limestone	Sand	Superplasticizer	Water
OPC	450.0			1350.0		225.0
UHPC	580.6	138.7	720.2	597.9	30.8	184.3

Table 2. The chloride ion content attached by simulated sea-sand.

			S0	S1	S3	S5	S7

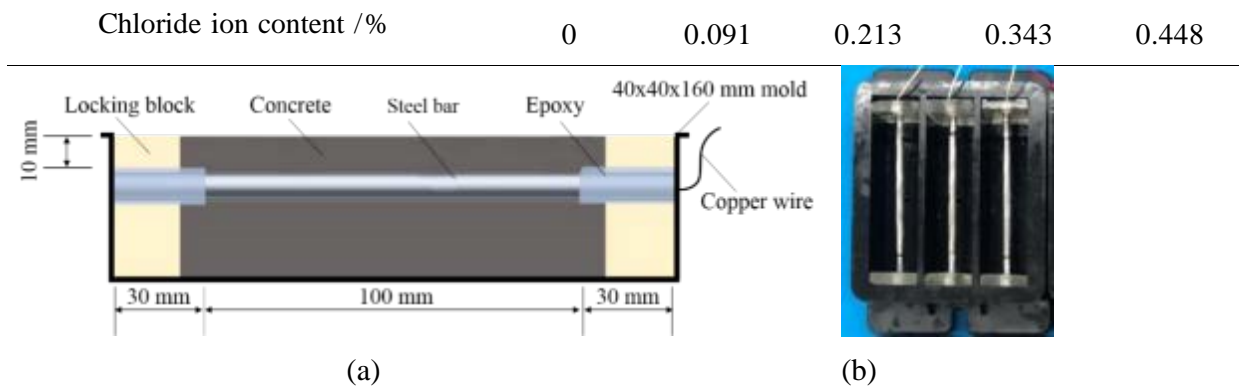| Chloride ion content /%	0	0.091	0.213	0.343	0.448

(a)   (b)

Fig 1. Schematic diagram (a) and physical map (b) of UHPC specimen

The specimen with a size of $40 \times 40 \times 160 \ mm^3$ for electrochemical tests is illustrated in Fig 1. The steel bar is HPB235. The diameter and exposed length of rebar embedded in UHPC is 6 mm and 100 mm, respectively; and the depth of cover layer is 10 mm.

3 Results and Discussion

3.1 Pore Structure

Fig 2 illustrates the pore structures of sea-sand UHPC at 3 d and 56 d. It is clear that the isothermal curves of all specimens show H3 hysteresis loop according to IUPAC classification, indicating that the pores in this range are dominated by flat slit structure, fracture and wedge structure. It observes that adsorption/desorption amounts of the early age specimens are much higher than those of the later age samples, especially for the U-S0-3 d sample, which means that the UHPC porosity is significantly reduced at later age, and the incorporation of sea-sand is beneficial to decrease the porosity at early age.

Due to the complexity of UHPC pore structure, the tensile strength effect is particularly prone to appear, resulting in the closure of hysteresis curve near the relative pressure of 0.45, as shown in Fig 2(a). Meanwhile, the "pseudo-peak" is observed around 4 nm using the data of desorption curves by BJH fitting method, shown in Fig 2(b), therefore, the adsorption curve data is more suitable for pore structure analysis in this study.
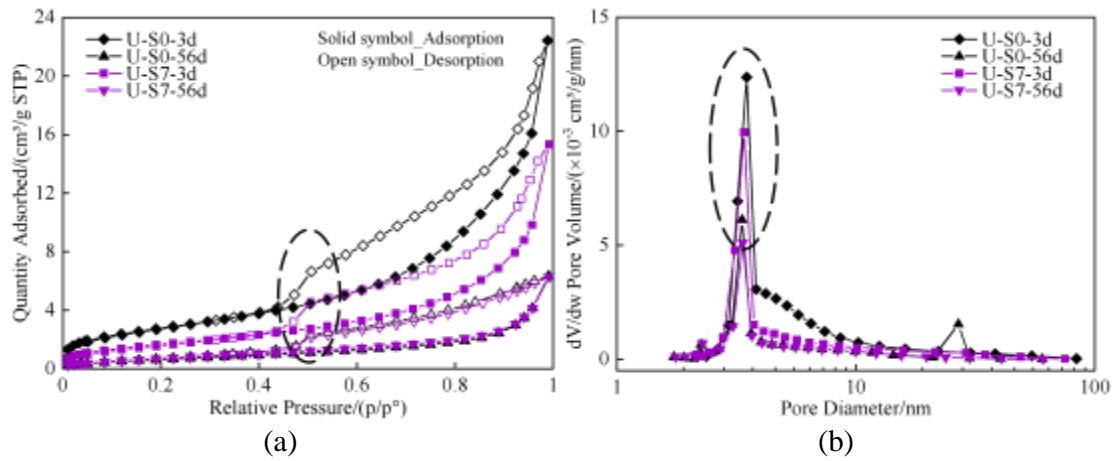
(a)   (b)

Fig 2. UHPC sample adsorption/ desorption isothermal curves （a）and pore structure analysis of desorption curves（b）.

3.2 Linear Polarization Measurement

Fig 3 compares the evolution of polarization resistance R_p and corrosion current density i_{corr} of reinforcement embedded in specimens at different immersion environments measured by linear polarization. As shown in Fig 3（a-1）and 3（b-1）, it can be seen that the R_p value of UHPC group is still on the rise after soaking in pure water and NaCl solution, and tends to be stable after about 60 days of immersion time. It is noteworthy that, the value of R_p is not sensitive to the chloride ion level. In the case of reinforcements in OPC specimens, the R_p soaking in NaCl solution decreases sharply faster than that in pure water within 60 days of exposure time, and it presents a continuous decline trend, while the measurement of R_p immersed in pure water remains stable at about 2000 kΩ cm^2 after 90 days of exposure time.
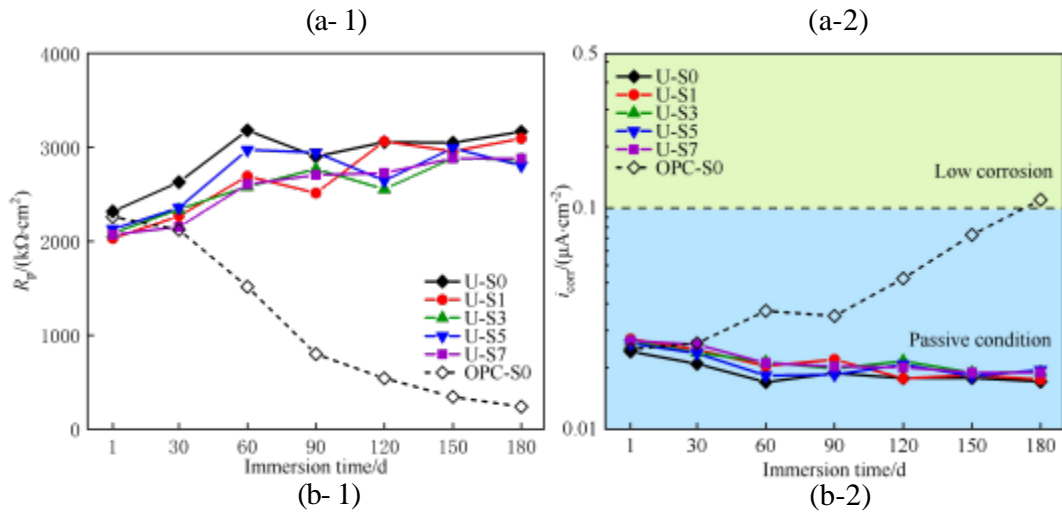
(a- 1)   (a-2)

(b- 1)   (b-2)
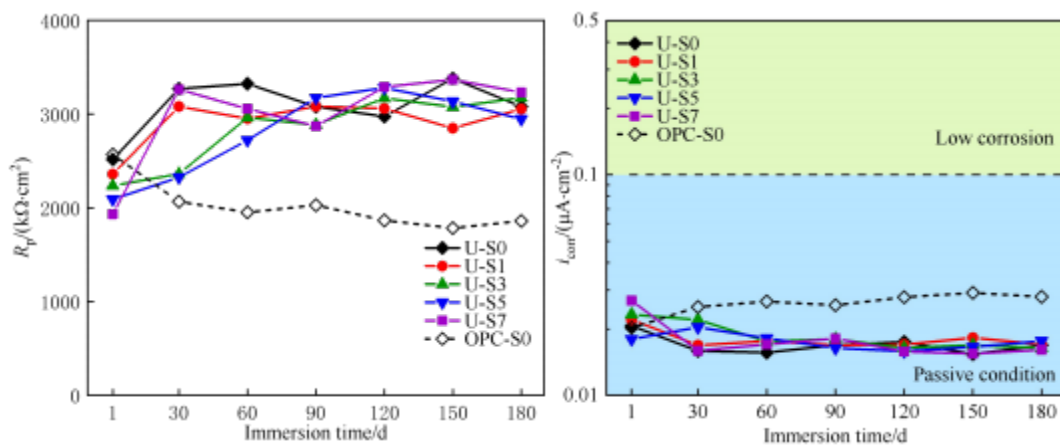
Fig 3. Evolution of R_p (1) and i_{corr} (2) of steel bars in samples immersed in water (a) and 3.5 wt.% NaCl solution(b).

The evolutions of corrosion current density i_{corr} are shown in Fig 3(a-2) and 3(b-2). It is noted that a Tafel constant B was required for the calculation of i_{corr} based on the Stern-Geary formula. However, the measurement of B through strong polarization had an adverse impact on the stability of formed passivation film, which could not guarantee the long-term reuse of the same rebar. Therefore, the empirical values of B (steel corrosion 26 mV, passivation 52 mV) was adopted in this study. It is found that the i_{corr} of rebar in UHPC group immersing in pure water and NaCl solution for a long time is hardly impacted by the endogenous chloride ion level, and remains at about 0.015 μA/cm^2 after 60 days which is at an extremely low corrosion rate. The i_{corr} in OPC specimens soaking in pure water slightly increases at the beginning of exposure, and then remains at about 0.025 μA/cm^2. However, the measurements of i_{corr} in OPC samples immersed in NaCl solution increases to around 0.01 μA/cm^2 at 180 d, which is in the low-speed corrosion stage.

3.3 Electrochemical impedance spectroscopy (EIS)
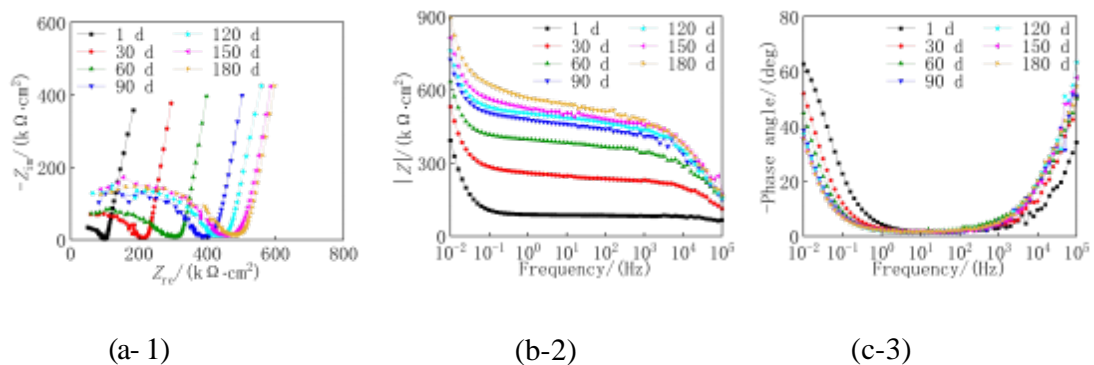

(a- 1)   (b-2)   (c-3)

Fig 4. Development of impedance plot in the form of Nyquist (a), Bode-Impedance (b) and Bode-Phase (c) for specimens of U-S7 immersed in pure water.
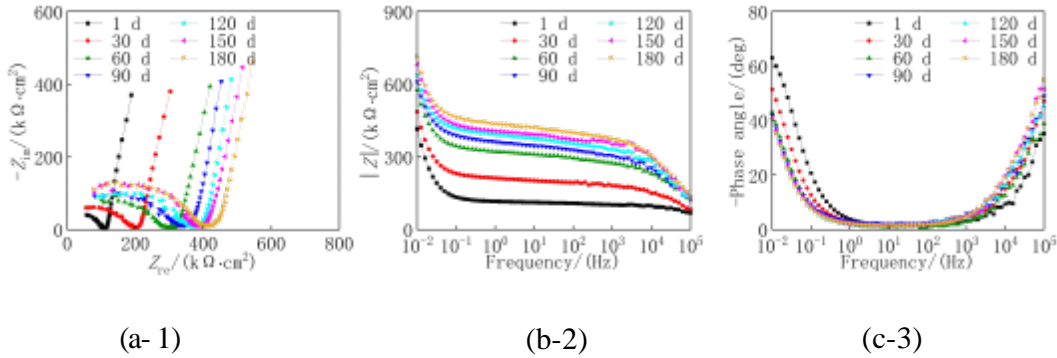

(a-1)   (b-2)   (c-3)

Fig 5. Development of impedance plot in the form of Nyquist (a), Bode-Impedance (b) and Bode-Phase (c) for specimens of U-S7 immersed in NaCl solution.

Fig 4 and 5 illustrates the EIS plots of UHPC samples up to 180 d at different immersion conditions. In generally, the spectra plots of UHPC samples are similar despite of the endogenous chloride content and immersion condition. For the UHPC groups, as shown in Fig 4(a-1) and 5(a-1), the Nyquist diagram comprises of two semi-circles. The semi-circle on the left is related to the properties of UHPC matrix, where the radius of semicircle tends to increase gradually, indicating the densification of UHPC matrix. The right semicircle characterizes the interface properties of steel bar, in which the radius of semi-arcs presents an upward trend with the increment of immersion age, signifying that the resistances of charge transfer and passive film have a long-term increasing trend.

In Fig 4(b-2), it is found that the impedance over the whole frequency range soaking in pure water increases greatly in the first 90 days, and then the impedance increases slightly. However, the impedance immersed in NaCl solution has evident increment before 60 d, and then remains basically unchanged, as illustrated in Fig 5(b-2), which is attributed to the stability of hydration process. The phase angle curves of UHPC are similar regardless of immersion environments and endogenous chloride levels, as shown in Fig 4 (c-3) and 5(c-3).

The ZsimpWin software is employed to fit the experimental data of OPC and UHPC groups. The Chi square error values are in the order of 10^{-4}, which indicates that the models are suitable for fitting data.
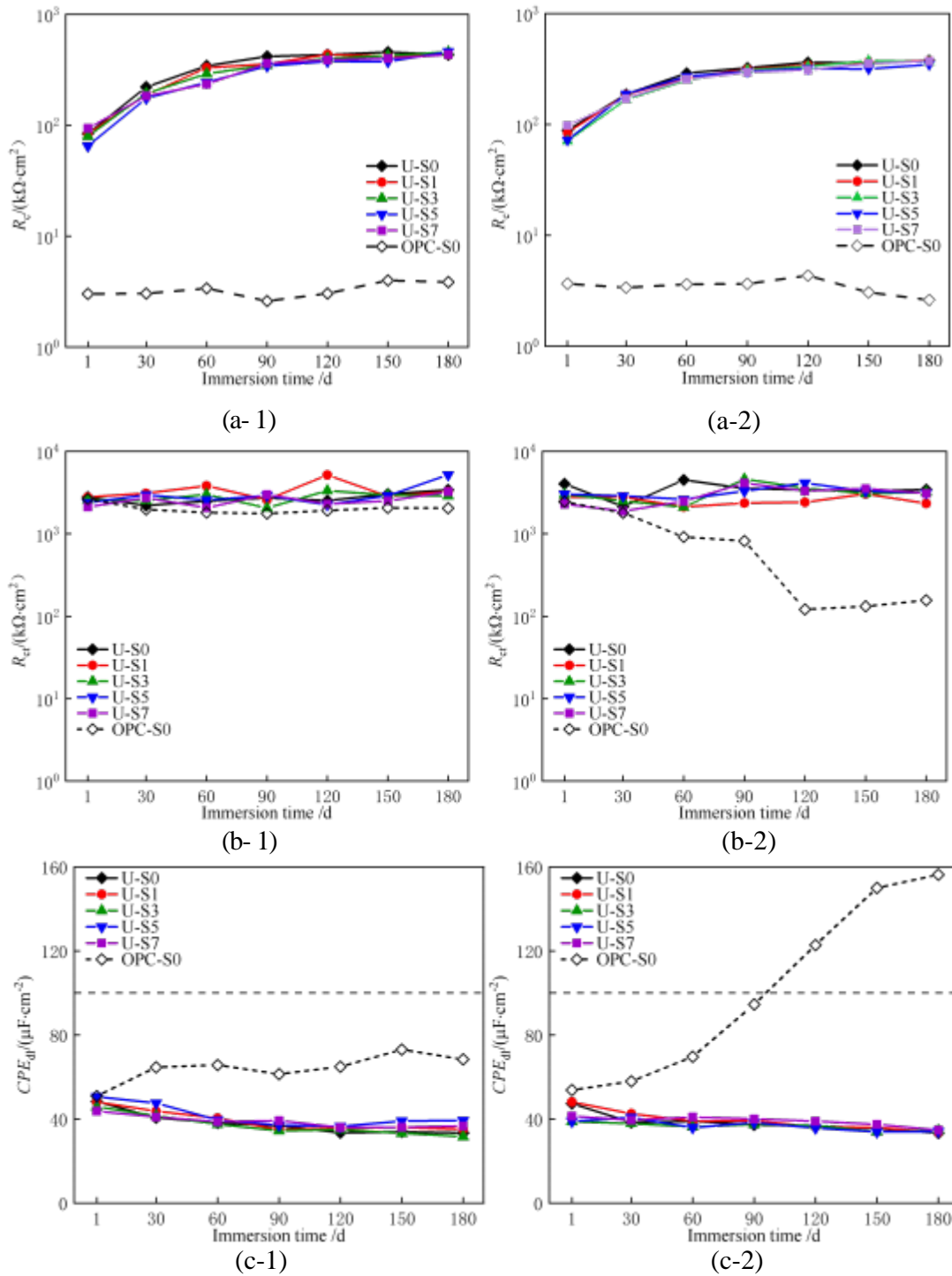
(a-1)   (a-2)

(b-1)   (b-2)

(c-1)   (c-2)

Fig 6. EIS fitting results of specimens immersed in pure water (1) and 3.5 wt.% NaCl solution (2): matrix resistance(a), charge transfer resistance(b), and electric double layer capacitance (c).

Fig 6 presents the EIS analysis results based on the proposed EEC models. It is clear that, as shown in Fig 6(a-1, a-2), despite of endogenous chloride levels, there is no

significant difference of matrix resistance of UHPC specimens between the soaking environments with pure water and NaCl solution. The matrix resistance of UHPC increases sharply in the first 90 days of immersion and then remains basically unchanged, indicating the slow formation of UHPC matrix microstructure which is associated with the hydration and pozzolanic reactions in UHPC.

Fig 6(b-1, b-2) illustrate the evolution of charge transfer resistance of rebar in UHPC and OPC immersed in pure water and NaCl solution, respectively. It should be noted that the charge transfer resistance is relevant to the corrosion rate of reinforcement. It is found that the rebar embedded in UHPC has an ultra-high resistance of charge transfer independent of the chloride ion level and the immersion environments, indicating the reinforcement in UHPC matrix is less likely to be corroded.

Fig 6(c-1, c-2) shows the evolution of electric double layer capacitance (CPEdl) fitting the electrolyte-steel interface, which is related to the roughness of passivation film. It is clear that the evolution of CPEdl representing UHPC is basically the same regardless of immersion environment and remains stable with the soaking age, which is similar to the abovementioned Rct development law. However, the capacitance evolution of OPC specimen immersed in pure water displaying a slight fluctuation, is higher than that of UHPC group, while the CPEdl soaking in NaCl solution increases sharply with the immersion age.

3.4 Cyclic polarization (CP)

Fig 6 compares the cyclic polarization curves of UHPC and OPC after 180 days of immersion in different conditions. It is found that the curves o all UHPC group with different endogenous chloride ion levels almost coincide, and the passivation zone of anodic polarization part extends from Ecorr to Epit, indicating that the steel bars in UHPC have essentially the same dynamic behavior, and remain in a stable passivation state at 180 d regardless of the immersion environment. In the case of OPC sample immersed in pure water as shown in Fig 6(a), compared to UHPC specimens, the cyclic polarization curves with a passivation zone is obviously shifted to the right, indicating that the pitting rate of reinforcement is slightly larger than that of UHPC group. However, regarding the OPC specimen soaking in NaCl solution, no passivation zone is observed in the cyclic polarization curve shown in Fig 6(b), suggesting that there is a high possibility of pitting corrosion risk of rebar in OPC. Furthermore, the direction of sweeping curve is different from that of other samples, forming a closed loop with the forward polarization curve, indicating that the steel bar has been corroded after 180 days of immersion in NaCl solution.
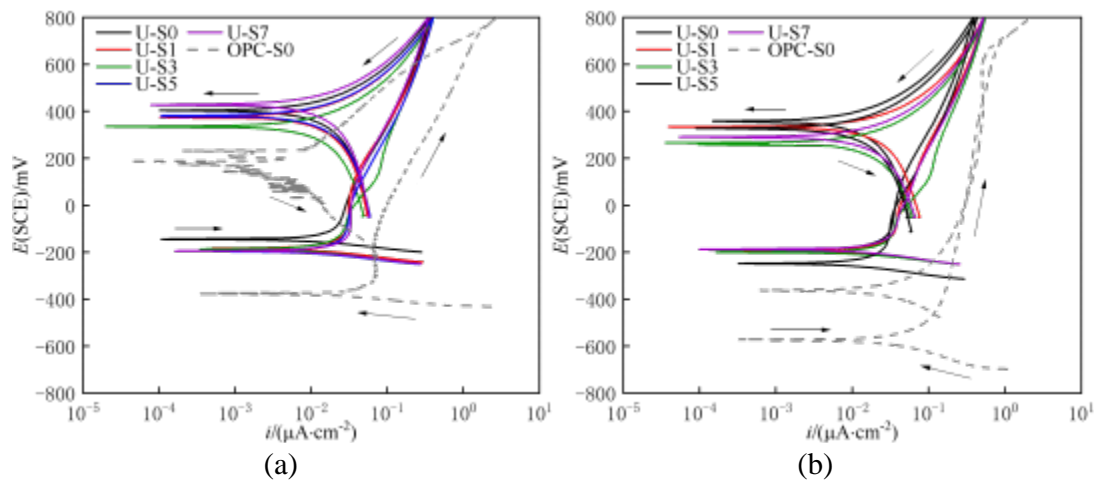
(a)   (b)

Fig 6. CP measurement curves of steel bars in UHPC and OPC after 180 days of immersion in pure water (a) and NaCl solution (b).

4 Conclusions

- The pore structure of UHPC is refined by incorporation of sea-sand in the early age, and is similar to that of ordinary UHPC at later age. The extremely dense microstructure of UHPC is conducive to protecting steel bars from corrosion.
- Regardless of the immersion environment, the probability of rebar corrosion in sea-sand UHPC is extremely low, where the Rp is greater than 250 kΩ·cm^2 and the icorr is less than 0.1 µA/cm^2. However, the lower Rp and higher icorr indicate that the steel bars in OPC soaking in NaCl solution are in the corrosion stage.

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