

Electrochemical impedance spectroscopy of concrete with nanoscale mineral additives

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The electrochemical impedance spectroscopy (EIS) tests of concrete with nanoscale mineral additives immersed in fresh water and saline water were carried out to analyze the effects of chloride ion conditions and nanoscale mineral additives on the impedance parameters of concrete. The results showed that at the same content of mineral impurities, the pore solution resistance, the resistance of charge transfer by hydration electrons and the diffusion impedance coefficient of concrete blocks immersed in saline water were less than those immersed in fresh water; the capacitance of a double electric layer was greater than that of concrete blocks immersed in fresh water, and the constant phase angle index was basically the same. This indicated that for concrete immersed in saline water, chloride ions diffuse into concrete; as a result, the free ion concentration in the pore solution and C-S-H gel increases, the resistance of the electrolyte in the pore solution and the diffusion resistance of free charge in the porous structure of concrete decrease. However, the presence of the chloride ion did not have a noticeable effect on the characteristics of the porous structure of concrete. Under the same immersion conditions, with an increase in the content of nanoscale mineral additives, the impedance parameters of concrete such as the pore solution resistance, the charge transfer resistance of hydration electrons, the diffusion impedance coefficient and the constant phase angle index showed an increasing trend, while the double electric layer capacitance basically remained unchanged, indicating that nanoscale mineral admixtures reduce the porosity of concrete, improve the compactness of concrete and improve performance of concrete.

Keywords: concrete, nanoscale mineral additives, chloride ion, electrochemical impedance spectroscopy, impedance parameter.

Електрохімічна імпедансна спектроскопія бетону з нанорозмірною мінеральною добавкою. *Yuxia Liang, Qiuyan Meng, Ruihong Jia*

Проведено випробування електрохімічної спектроскопії імпедансу (EIC) бетону з нанорозмірними мінеральними добавками, зануреними у прісну та солону воду. Результати показали, що при однаковому вмісті мінеральної домішки опір розчину пор, опір перенесення заряду електронами гідратації і коефіцієнт дифузійного опору бетонних блоків, занурених в солону воду, менше, ніж занурених у прісну воду. Електрична ємність була більшою, ніж у бетонних блоків, занурених у прісну воду, а показник постійного фазового кута був переважно таким самим. Це вказує на те, що для бетону, зануреного в солону воду, іони хлориду дифундують в бетон, що збільшує концентрацію вільних іонів у розчині пор та гелі C-S-H. Однак присутність хлорид-іону не впливає помітно на характеристики пористої структури бетону. У тих же умовах занурення, зі збільшенням нанорозмірних мінеральних домішок, параметри імпедансу бетону, такі як опір розчину пор, опір перенесення заряду електронів гідратації, коефіцієнт дифузійного імпедансу та індекс постійного фазового кута мають тенденцію до збільшення, в той час як електроємність практично не змінилася. Це вказує на те, що нанорозмірна мінеральна добавка знижує пористість бетону, покращує його щільність та покращує робочі характеристики бетону.

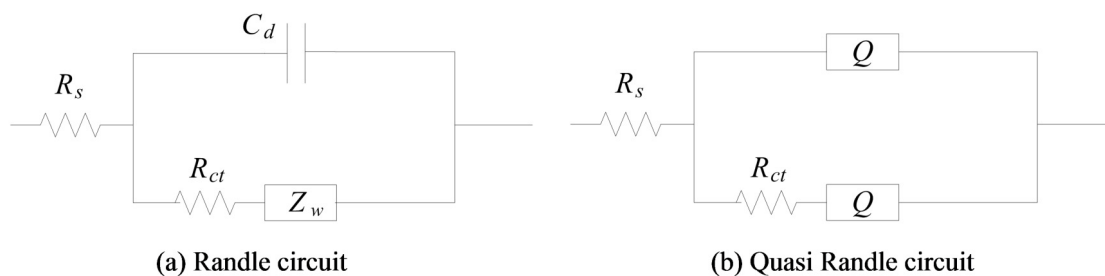


Fig. 1. Equivalent circuits of concrete: (a) the Nyquist plot of the Randle circuit; (b) the Nyquist plot of the quasi-Randle circuit.

1. Introduction

With the development of science and technology, nano materials technology is more and more widely used in concrete materials. Nanoscale ultra-fine fly ash, slag and other industrial residue are added into concrete as mineral additives, which not only realizes the sustainable use of materials, turns waste into treasure and reduces the use of cement, but also improves the working performance of concrete and improves the durability of concrete [1–2]. Therefore, an in-depth study of the effect of nanoscale ultra-fine fly ash and slag on the microstructure and properties of concrete can not only promote the rational utilization of nanoscale ultra-fine fly ash and slag, but also have important significance for improving the working performance of concrete. At present, the research of concrete with nanoscale mineral additives mainly focuses on the effect of the additive on macro-performance and mechanical properties of concrete [3–5], such as permeability, strength and so on. There are few studies on the change of internal microstructure of concrete with nanoscale ultra-fine mineral additives [6], and fewer studies on micro-characteristics of concrete with nanoscale mineral additives in an aggressive environment. Based on the measurement of impedance spectrum parameters of concrete with nanoscale ultra-fine mineral additives immersed in saline water and fresh water, the impedance parameters and internal micro-structure changes of concrete with nanoscale ultra-fine mineral additives in a chloride environment are studied [7], which provides a reference for the durability study of concrete with nanoscale ultra-fine mineral additives.

2. Experimental

2.1 Physical significance of impedance spectrum and impedance parameters of concrete

Electrochemical impedance spectroscopy is an important tool for studying the microstructure and properties of materials. As a porous medium material, concrete can be regarded as a special electrochemical system with an electrolyte solution in pores. The electrochemical impedance spectra (EIS) of concrete can be measured by placing inert metal electrodes on the opposite sides of concrete blocks. According to the change of EIS, the development and change of concrete microstructures can be understood. Under ideal conditions, the Nyquist diagram of a concrete EIS is of the Randles type, but in practical application, due to the special structure system of concrete, the Nyquist diagram of a concrete EIS is of the quasi-Randles type. Fig. 1 shows the Nyquist graphs of the Randles type and the quasi-Randles type; and Fig. 2 shows equivalent circuits of the Randles type and the quasi-Randles type. The difference between the Nyquist graphs of the Randles type and the quasi-Randles type is in the follows:

(1) The electrical double layer capacitance C_d in the Randles equivalent circuit is replaced by a constant phase angle element (CPE).

(2) In the Faraday impedance, the Warburg impedance Z_w is also replaced by a constant phase angle element. The angle of intersection between the low-frequency sloped line of the spectrum and the real axis deviates by 45° .

In this paper, the quasi-Randles equivalent circuit shown in Fig. 1b, and Fig. 2b is used for analysis. The physical meanings of electrochemical parameters of R_s , R_{st} , C_d , q , σ , and p are as follows.

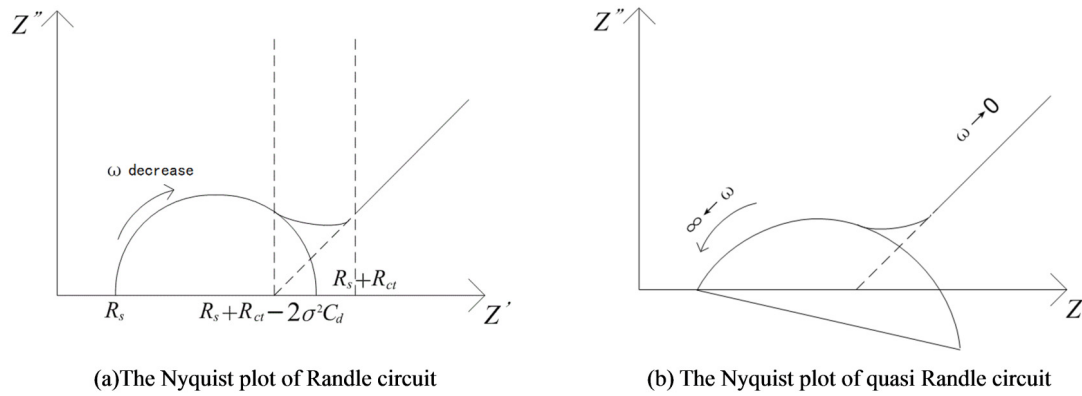


Fig. 2. The Nyquist plot.

(1) R_s is the resistance of electrolyte in a concrete pore solution, and the unit is $\Omega \cdot \text{cm}^2$. According to the quantitative relationship between electrochemical impedance parameters and structural parameters, is inversely proportional to the total ion concentration in porous solution and to the total porosity of concrete.

(2) C_d is the double electric layer capacitance of C-S-H gel, indicating the electrical properties of cement hydration product, and the unit is F/cm^2 . In the quasi-Randles equivalent circuit, it is always replaced by a constant phase angle element CPE, which is expressed as $C_d = K(j\omega)^{-q}$. The size of can be used to represent the size of C_d , and the index q denotes the degree of flattening of the high-frequency semicircle.

(3) R_{ct} is the resistance of electrons in a C-S-H hydrated gel for carrying out a charge reaction, reflecting the characteristics of the activation process. The unit is $\Omega \cdot \text{cm}^2$.

(4) Diffusion impedance Z_w ($Z_w = \sigma(j\omega)^{-1/2}$, σ is diffusion impedance coefficient) reflects the characteristics of the diffusion process and is replaced by a constant phase angle element (CPE) in the quasi-Randles equivalent circuit, which is expressed as $Z_D = Q(j\omega)^{-p}$ ($0 < p < 1$). The diffusion impedance coefficient $\sigma(\text{K}\Omega\text{S}^{-1/2})$ can still be used to describe the resistance of concrete pore solution ions to diffusion in a porous medium. The constant phase angle index p is related to the pore structure characteristics of the cement paste in concrete, which reflects the subtle changes of the pore structure of concrete. The fractal dimension d indicates the complexity and compactness of the characteristics of the pore structure. The relationship between the constant phase angle index p and the fractal

dimension d is $d = 4 - p$. The larger the constant phase angle index p , the smaller the fractal dimension d , and the closer the structure to the dense three-dimensional system. Therefore, the constant phase angle index p can also be used to express the complexity and compactness of concrete pore structure [8–11].

2.2 Specimen preparation and testing

Ordinary Portland cement PO42.5r produced by Dalian Xiaoyetian Cement Co., Ltd. was used as cement. As a fine aggregate, high-quality river sand was used, belonging to the II gradation zone with a fineness modulus of 2.5. High quality crushed limestone of continuous gradation was used as a coarse aggregate. In nanoscale slag, an ultrafine mineral powder ground for 100 minutes, with a specific surface area more than 550 m^2/kg and an average particle size of less than 90 nm was used. The nanosized fly ash ground for 60 minutes had a specific surface area over 550 m^2/kg and an average particle size of less than 90 nm. Water was distilled water. The mixing ratio of concrete specimens is shown in Table 1. In the table, C1 is concrete without mineral admixture (ordinary concrete), F1 ~ F4 are concrete with different content of ultra-fine fly ash, K1 ~ K4 are concrete with different ultra-fine slag admixture, and KF1 ~ KF4 are concrete with ultra-fine slag and fly ash at the same time.

Six concrete cubic specimens (100 mm×100 mm×100 mm) with a water-gel ratio of 0.5 and different ultra-fine mineral additives were prepared. The specimens were cured in a standard curing room for 28 days. After that, two opposite sides of the specimen were coated with epoxy resin for sealing. The rest of the opposite sides were kept as working faces. From the numbered samples, 3 concrete samples were

Table 1. Mixing proportion of concrete

Number	Water-gel ratio	Gel material content, kg/m ³	Gel material percent			Water, kg/m ³	Sand, kg/m ³	Broken stone, kg/m ³
			Cement, %	fly ash, %	Slag, %			
C1	0.5	445	100	0	0	222	222	1157
K1	0.5	445	90	0	10	222	222	1157
K2	0.5	445	80	0	20	222	222	1157
K3	0.5	445	70	0	30	222	222	1157
K4	0.5	445	60	0	40	222	222	1157
F1	0.5	445	90	10	0	222	222	1157
F2	0.5	445	80	20	0	222	222	1157
F3	0.5	445	70	30	0	222	222	1157
F4	0.5	445	60	40	0	222	222	1157
KF1	0.5	445	60	10	30	222	222	1157
KF2	0.5	445	60	20	20	222	222	1157
KF3	0.5	445	60	10	30	222	222	1157

taken and immersed in a NaCl solution with a concentration of 3.25 %. Attention should be paid to the contact of the working face with salt water. The remaining concrete specimens were immersed in fresh water (tap water), and the working face was in contact with fresh water. The EIS of specimens with different immersion time (0d, 7d, 14d, 21d, 28d, 60d, 90d and 150d) were measured on an RST electrochemical workstation produced by Zhengzhong Shiruisi Science and Technology Instrument Co., Ltd. The experimental data were analyzed and processed by ZsimpWin and Origin software, and the impedance parameters of meso-structure characteristics of concrete with mineral admixture under different immersion conditions were obtained, namely R_s , R_{st} , C_d , q , σ and p .

3 Results and discussion

3.1 Analysis of impedance parameters of concrete with nanoscale ultra-fine fly ash

(1) Parameter R_s

R_s is the resistance of electrolyte in a concrete pore solution, which is inversely proportional to the total number of ions in the pore solution and the total porosity of concrete. In the pore solution of ordinary concrete and concrete with ultra-fine mineral additives under non-immersion conditions, the main ions are OH^{-1} , K^{+} and so on, and the concentration of ions in the pore solution remains stable at an early stage of sample formation. It can be seen from Fig. 3a that for concrete with the same mixing ratio, the resistance R_s of an electrolyte in the pore solution of the cement

paste immersed in saline water is less than that of the test block immersed in fresh water. With an increase in the immersion time, this difference becomes larger. This is due to the fact that for the concrete specimen immersed in saline water, chloride ions diffuse into concrete, and there are not only OH^{-1} and K^{+} ions in the pore solution but also diffused Cl^{-1} . Therefore, the total amount of ions in the pore solution of concrete immersed in saline water increases. For the specimen immersed in fresh water, the ingress of water does not increase the amount of ions in the porous solution. Therefore, the resistance R_s of electrolyte in the pore solution of the concrete cement paste immersed in saline water is less than the resistance of concrete immersed in fresh water. With an increase in the immersion time, the amount of chloride ions diffused into the solution increases, and the difference in the resistance R_s of the electrolyte in the solution increases. As can be seen from Fig. 3a, for the concrete specimen immersed in fresh water or saline water, with an increase in the immersion time and the content of ultra-fine fly ash, the resistance of the electrolyte in the concrete pore solution increases. This is due to the fact that under conditions of the same quality of the gel material, the ultra-fine fly ash has a larger specific surface area, larger material activity and a smaller particle size, which can play the role a filler and compaction and reduce the porosity of concrete. With an increase in the content of the ultra-fine fly ash additive, the filling and compaction effects are more obvious, and the R_s value is larger.

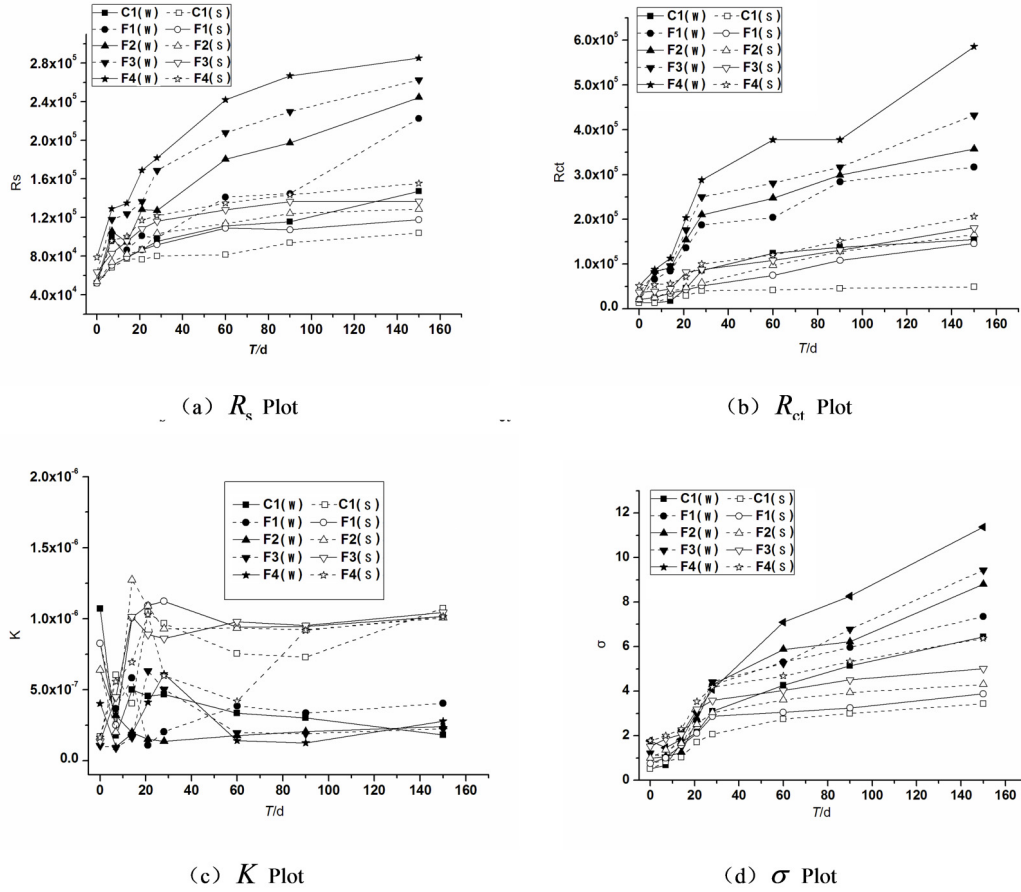


Fig. 3. Electrochemical parameters of concrete with nano level fly ash.

(2) Parameter R_{ct}

The parameter R_{st} is the resistance of free electrons of the C-S-H gel to charge transfer. From Fig. 3b, it can be seen that for the test specimens with the same amount of ultra-fine fly ash, the resistance of the specimen immersed in saline water is significantly less than that of the specimen immersed in fresh water, indicating that the chloride ions in saline water diffused into the C-S-H gel increase the number of ions in the C-S-H gel, reduces resistance to charge transfer by hydration electrons, and changes the electrical properties of the C-S-H gel. At the same time, from Fig. 3b, it can be seen that for the concrete specimens under the same conditions, the value of R_{st} increases with an increase in the content of ultra-fine fly ash, indicating that ultra-fine fly ash in the test specimen undergoes a secondary hydration reaction, and more C-S-H gel is formed, which reduces the porosity of the concrete.

(3) Parameter C_d

The value C_d is the capacitance of the C-S-H gel in concrete. In this paper, K and q are used to characterize the capacitance of a double electric layer. From Fig. 3c, it can be seen that for the specimens with the same ultra-fine fly ash content, the K value of the specimen immersed in saline water is greater than that of the specimen immersed in fresh water. This is because the chloride ions in the saline water diffuse into the C-S-H gel, increasing the ion concentration of the C-S-H gel, thereby increasing the capacitance of the C-S-H gel. It can also be seen from Fig. 3c that under the same immersion conditions, the K value of concrete with ultrafine fly ash is not much different from that of conventional concrete, and the amplitude of K change is not obvious with increasing immersion time, indicating that the addition of fly ash has little effect on the electrical properties of the C-S-H gel. After curing and forming the test specimen, the internal structure of the concrete is gradually compacted. The constant phase angle index q of ordinary concrete is close to 1. The study shows that the internal

Table 2. CPE index p of concrete with different nano-level fly ash

D	C1		F1		F2		F3		F4	
	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water
0	0.80	0.80	0.81	0.81	0.83	0.83	0.85	0.85	0.85	0.85
7	0.83	0.79	0.82	0.81	0.84	0.83	0.84	0.83	0.85	0.84
14	0.86	0.82	0.85	0.82	0.82	0.84	0.85	0.84	0.84	0.82
28	0.85	0.83	0.87	0.83	0.85	0.84	0.86	0.85	0.88	0.84
60	0.86	0.85	0.88	0.85	0.86	0.84	0.86	0.85	0.88	0.84

structure of concrete with ultrafine fly ash is denser than for ordinary concrete, and the constant phase angle index q is closer to 1. If the numerical difference in the q index is very small, the influence of the C-S-H gel on capacitance is very limited; so the q index can approach that of the constant phase angle of concrete, $q = 1$.

(4) Diffusion impedance coefficient σ

The diffusion impedance coefficient σ represents the resistance to diffusion of ions in the porous medium of the hardened cement paste; this is due to the concentration of ions and the characteristics of the porous structure of the concrete porous solution. From Fig. 3d, it can be seen that for the specimen with ultra-fine fly ash, the σ value of the specimen immersed in saline water is less than that of the specimen immersed in fresh water. This is because chloride ions in saline water diffuse into the pore solution of concrete, increase the ion concentration of the pore solution of concrete, thereby reducing the diffusion impedance coefficient σ . It can also be seen from Fig. 3d that under the same immersion conditions, the diffusion impedance coefficient σ increases gradually with increasing immersion time and the content of ultra-fine fly ash; this indicates that the filling effect and compaction effect of ultra-fine fly ash reduce the porosity of the concrete, and then increase the diffusion impedance coefficient σ .

The constant phase angle index p and fractal dimension d satisfy the relation $d = 4 - p$ in numerical value, therefore, can be used to describe the pore structure characteristics of concrete. The larger p is, the closer the pore structure of concrete is to the dense three-dimensional system. The denser the structure is, the more difficult the diffusion of ions. From Table 2, it can be seen that with the same amount of ultra-fine fly ash, the constant phase angle index of concrete does not differ significantly in salt and fresh water, which indicates that

the chloride ion does not have a clear effect on the pore structure of concrete. The constant phase angle index p of concrete with ultra-fine fly ash is larger than that of ordinary concrete, which indicates that the concrete with ultra-fine fly ash has a denser structure.

3.2 Analysis of the impedance parameter for concrete with nanoscale ultra-fine slag

(1) Parameters R_s and σ

From Fig. 4a and Fig. 4d, it can be seen that for the concrete with the same ultra-fine slag, the impedance parameters R_s and σ of the slag concrete immersed in saline water are less than those of the same concrete immersed in fresh water, and the variation law is the same as that for concrete with ultra-fine fly ash. The results show that for the specimen immersed in saline water, chloride ions diffuse into the pore solution of slag concrete, increasing the total amount of ions in the pore solution, thus reducing the impedance parameters of the slag concrete. It can also be seen from Figs. 4a and 4d that for slag concrete under the same immersion conditions, the impedance parameters increase with immersion time and ultrafine slag content, indicating that the ultrafine slag has a filling and compacting effect and reduces the porosity of the concrete.

From Table 3, it can be seen that the constant phase angle index p of concrete with the same ultra-fine slag content in saline water and fresh water is the same. According to the relationship $d = 4 - p$ between the constant phase angle index p and fractal dimension d , it can be judged that chloride ions diffuse into slag concrete, which has no obvious effect on pore structure characteristics of the slag concrete, but only increases the ion concentration in the concrete. At the same time, the constant phase angle index p of slag concrete is larger than that of ordinary concrete, which indicates that ultra-fine slag concrete has a more compact structure.

Table 3. CPE index p of concrete with different contents of nano-level slag

d	C1		K1		K2		K3		K4	
	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water
0	0.82	0.82	0.83	0.81	0.83	0.81	0.85	0.85	0.85	0.85
7	0.83	0.83	0.84	0.83	0.84	0.83	0.81	0.83	0.85	0.86
14	0.86	0.85	0.85	0.86	0.84	0.86	0.86	0.84	0.83	0.83
28	0.85	0.83	0.87	0.85	0.85	0.84	0.86	0.85	0.88	0.87
60	0.85	0.86	0.87	0.86	0.88	0.87	0.89	0.91	0.91	0.90

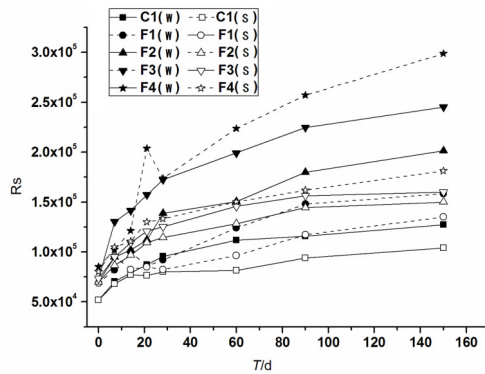
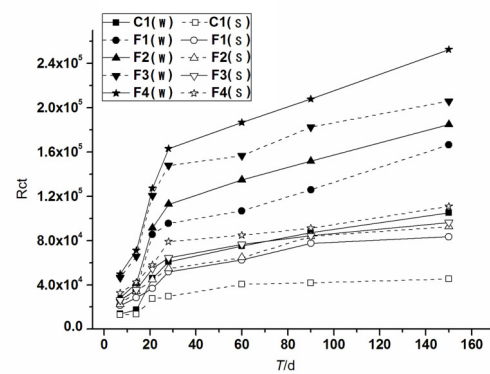
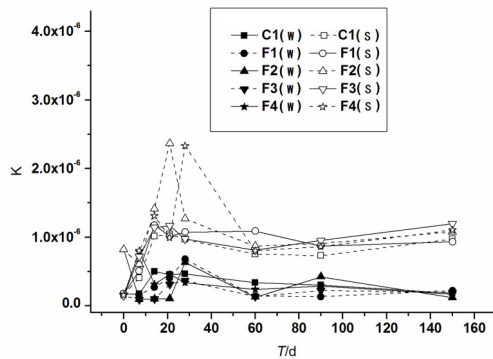
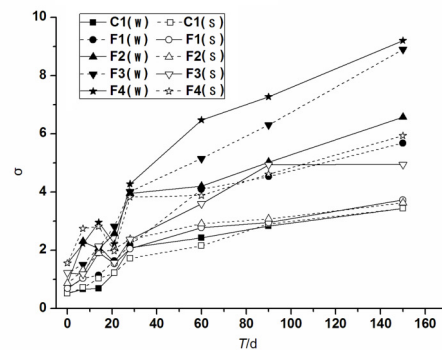
(a) R_s Plot(b) R_{ct} Plot(c) K Plot(d) σ Plot

Fig. 4. Electrochemical parameters of concrete with nano-level slag.

(2) Parameters R_{ct} and K

It can be seen from Fig. 4b and Fig. 4c that for the concrete specimen with the same mixing ratio, the impedance parameter R_{ct} of the specimen immersed in fresh water is greater than that of the specimen immersed in saline water, and the impedance parameter K of the specimen immersed in fresh water is smaller than that of the specimen in saline water. The reason is that for the specimen immersed in saline water, chloride ions diffusing into the C-S-H gel increase the number and variety of free ions

in the C-S-H gel; thus, the resistance R_{ct} of hydrated electrons to the charge transfer is reduced and the capacitance electricity of C-S-H gel increases. It can be seen that chloride ions diffuse into the C-S-H gel of slag concrete and changes the electrical properties of the C-S-H gel.

Fig. 4b and Fig. 4c also show the changes of impedance parameters R_{ct} and K of concrete with different ultra-fine slag content in the same soaking environment. It can be seen that the impedance parameter R_{ct} increases with increasing slag content, which

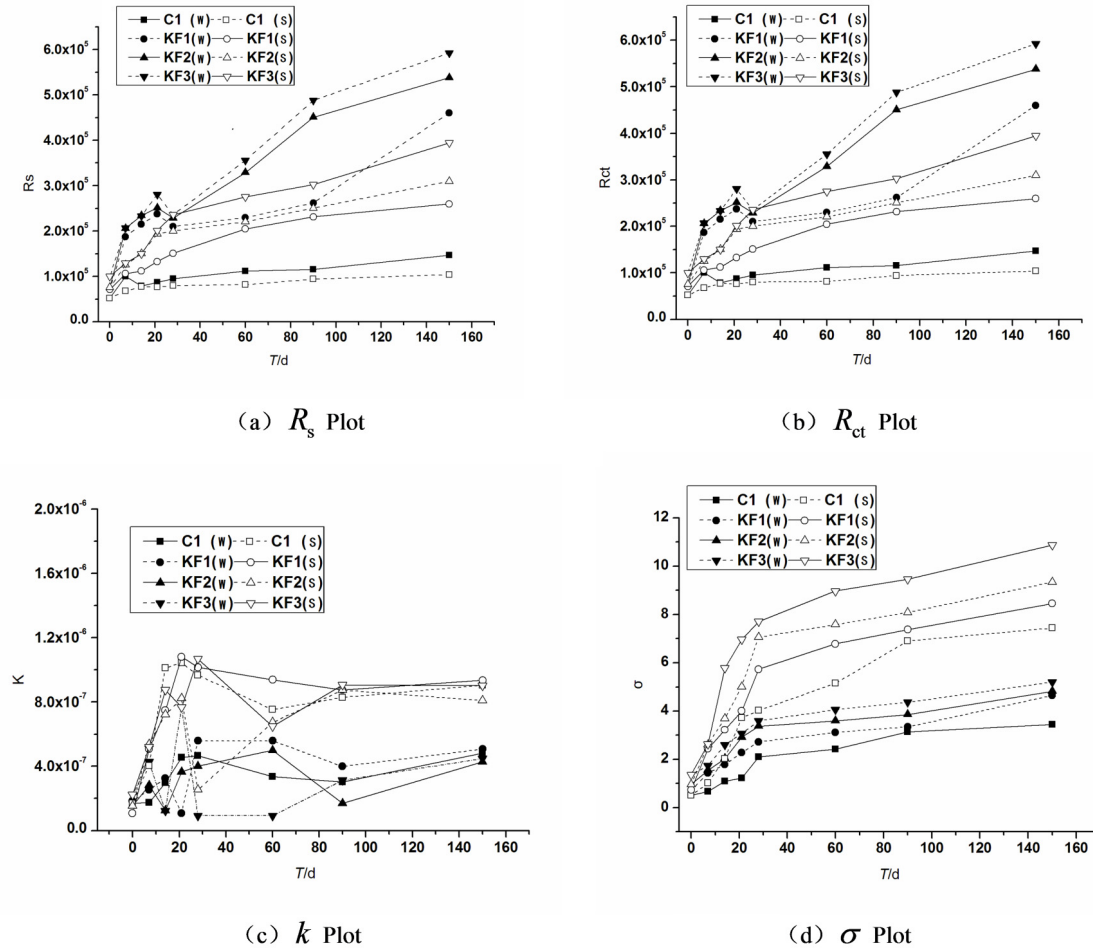


Fig. 5. Electrochemical parameters of composite concrete at different soak periods.

indicates that the slag content affects the pore structure of concrete and reduces the porosity of the concrete. The impedance parameter K does not change significantly with the slag content, which indicates that the addition of ultra-fine slag has little effect on the electrical properties of concrete C-S-H gel.

3.3 Analysis of impedance parameters of composite concrete with nanoscale ultra-fine slag/fly ash

(1) Parameters R_s and σ

Fig. 5a and Fig. 5d show the R_s and σ values of ultra-fine slag/fly ash composite concrete immersed in fresh water and saline water (the total content of ultrafine slag and fly ash is the same as in concrete mixed only with ultrafine slag and only fly ash). As can be seen from the figure, for the concrete specimens with the same ultra-fine slag/fly ash content, the impedance parameters R_s and σ of the specimens immersed in saline water are smaller than those of speci-

mens immersed in fresh water. This is because for the specimen immersed in saline water, chloride ions diffuse into the pore solution of the composite concrete; as a result, the species and concentration of ions increase in the pore solution, and the diffusion of ions in the pore structure decreases. It can also be seen from Fig. 5a and Fig. 5d that in the same immersion environment, the impedance parameters R_s and σ of the composite concrete gradually increase with increasing immersion time and slag content. Their numerical values are obviously larger than those of ordinary concrete, and are also larger than those of the concrete with only fly ash in the same amount and the concrete with only slag in the same amount in Fig. 3a,d and Fig. 4a,d. This shows that the micro-structure of ultra-fine slag/fly ash composite concrete is more compact and the porosity and average pore diameter are smaller than those of concrete with only ultra-fine fly ash in the same amount and

Table 4. CPE index p of composite concrete in salt water

d	C1		KF1		KF2		KF3	
	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water	Fresh water	Saline water
0	0.82	0.82	0.84	0.85	0.84	0.83	0.82	0.81
7	0.84	0.86	0.88	0.83	0.85	0.84	0.86	0.83
14	0.85	0.85	0.86	0.86	0.87	0.86	0.85	0.86
28	0.85	0.85	0.89	0.88	0.88	0.87	0.86	0.87
60	0.86	0.87	0.89	0.91	0.88	0.90	0.89	0.90

concrete with only the ultra-fine slag in the same amount.

From Table 4, it can be seen that the constant phase angle index p of composite concrete with the same content of additives when immersed in saline water and fresh water differs little, which indicates that chloride ion diffusion only increases the ion concentration inside the composite concrete, and does not have a noticeable effect on the characteristics of the porous structure of the composite concrete. At the same time, the constant phase angle index p of the composite concrete is larger than that of ordinary concrete, and also larger than that of concrete with only ash in the same amount and concrete with only slag in the same amount (Table 2 and Table 3). It shows that the micro-structure of the ultra-fine slag/fly ash composite concrete is closer to a dense three-dimensional system than that of concrete with only fly ash in the same amount and concrete with only slag in the same amount.

(2) Parameters R_{ct} and σ

Fig. 5b and Fig. 5c show the parameters R_{ct} and K of slag/fly ash composite concrete with different immersion time in fresh water and saline water. It can be seen from the figure that under the same mixing ratio, the impedance parameter R_{ct} of the composite concrete specimen immersed in saline water is smaller than that of the specimen immersed in fresh water; while the impedance parameter K is larger than that of the specimen immersed in fresh water, indicating that chloride ion diffusing into the C-S-H gel of the composite concrete increase the ion concentration in the gel and change the electrical properties of the C-S-H gel. Under the same immersion conditions, the impedance parameter R_{ct} of the composite concrete is larger than that of ordinary concrete, and also larger than that of concrete with only fly ash in the same amount and concrete with only slag in the same amount (Fig. 3b and Fig. 4 b; this

indicates that the structure of the composite concrete is more compact with the same amount of the additive.

4 Conclusions

In this paper, the EISs of concrete with nanoscale mineral additives of ultra-fine slag and the ultra-fine fly ash when immersed in fresh water and saline water were studied, and the following conclusions are drawn:

(1) For the concrete with the same nanoscale ultra-fine mineral additive, the electrolyte resistance R_s , the resistance R_{st} of charge transfer of electrons during hydration, and the diffusion impedance coefficient of the specimens immersed in saline water are all smaller than those of the specimens immersed in fresh water. The double electric layer capacitance C_d is larger than that of the specimen immersed in fresh water, and the constant phase angle index p is basically the same, indicating that in the presence of chloride ions, the resistance of concrete decreases, the ion and free charge transfer in pore structure is easier, and the electrical activity of concrete is greater. If there are reinforcing bars in concrete, the risk of corrosion of the reinforcing bars is increased.

(2) Under the same immersion conditions, with an increase in the nanoscale mineral additive content, the electrolyte resistance R_s , the resistance R_{st} of charge transfer of electrons during hydration reaction and the diffusion impedance coefficient σ in the concrete pore solution gradually increase, while the double electric layer capacitance C_d remains unchanged, indicating that compared with ordinary concrete, the concrete with nanoscale ultra-fine mineral additives has lower porosity and higher compactness.

(3) The porosity and average pore diameter of the composite concrete with both nanoscale ultra-fine slag and fly ash are smaller and the concrete is denser than the

concrete only with ultra-fine slag or the ultra-fine fly ash in the same content.

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References

1. M.Alkaysi, S.El-Tawil, Z.Liu, *Cement Concrete Composit.*, **66**, 47 (2016).
2. M.Otieno, H.Beushausen, M.Alexander, *Cement and Concrete Composites*, **46**, 56 (2014).
3. W.C.Choi, S.W.Kim, S.J.Jang, H.D.Yun, *Magazine Concrete Res.*, **69**, 402 (2017).
4. Q.Ma, R.Guo, K.He et al., *Magazine Concrete Res.*, **70**, 1243 (2018).
5. Jiang Fengjiao, Yu Gongzhi, Liang Ce et al., *Funct.Mater.*, **28**, 114 (2021).
6. P.Hou, S.Kawashima, K.Wang et al., *Cement Concr Compos.*, **35**, 12 (2013).
7. Lian Zibao, *Funct.Mater.*, **29**, 559 (2022).
8. Zhang Rui, Cheng Xin, Hou Pengkun et al., *Constr.Build.Mater.*, **81**, 35 (2015).
9. W.C.Choi, S.W.Kim, S.J.Jang, H.D.Yun, *Magazine Concrete Res.*, **69**, 347 (2017).
10. H.Eskandari, M.Vaghefi, K.Kowsari, *Proc. Mater. Scien.*, **11**, 594 (2015).
11. Schabowicz Krzysztof, Ranachowski Zbigniew, *Constr.Build.Mater.*, **110**, 182 (2016).