

Short Communication

## Usability of Conductive based Cement Anode for Impressed Current Cathodic Protection of Reinforced Concrete Structures

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The service life of an impressed current cathodic protection (ICCP) system for reinforced concrete structures is primarily determined by the serviceability of the anode used. In this paper, a long-term galvanostatic polarization test was conducted to investigate the serviceability and durability of a cement conductive anode, and then the microcosmic surface topography and the phase components of the polarized and unpolarized cement anodes were analysed. The results indicate that the long-term operation of the cement anode can cause the formation of Friedel's salt, the reaction of calcium hydroxide crystals, the electrochemical oxidation of the conductive admixtures, and the damage to the interface between the primary anode and the cement conductive anode. Additionally, the electrochemical oxidation of conductive admixtures added into the cement anode is found to be the fundamental reason for the loss of the serviceability of the cement conductive anode, and the model predicting the life expectancy of the cement conductive anode is also presented.

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**Keywords:** reinforced concrete structures; impressed current cathodic protection; cement conductive anode; serviceability

### 1. INTRODUCTION

The corrosion of reinforced steel severely degrades the durability and safety of reinforced concrete (RC) structures, which are the primary structure style in the field of civil engineering [1-4]. With the deterioration of the global climate and environment, the corrosion of RC structures will become an increasingly serious problem [5]. Consequently, many research communities and engineers are urgent to find an effective method to control the corrosion of RC structures. Over the past few decades, many

methods have been developed to inhibit or prevent the corrosion of reinforced steel [6-9], such as electrochemical realkalization (ERA), electrochemical chloride removal (ECR), cathodic protection (CP), anticorrosion painting, corrosion inhibitors, and high-performance concrete. However, CP, which includes impressed current cathodic protection (ICCP) and sacrificial anode cathodic protection (SACP), is a type of directly controlling corrosion technique, and has been demonstrated as a very effective and reliable method [10-13]. For these two types of CP, a polarizing electrical current is required to deliver the protected reinforcing steels. In SACP, the polarizing current is produced by linking a more active metal with the protected steel bar [14]; in ICCP, the polarizing current is provided by the circuit consisting of an external power supply, an auxiliary anode system and the protected steel bar [15]. Compared with SACP, ICCP is more suitable for some large structural engineering projects with a long-life expectancy because it can provide a long term and sufficient polarizing electrical current [16].

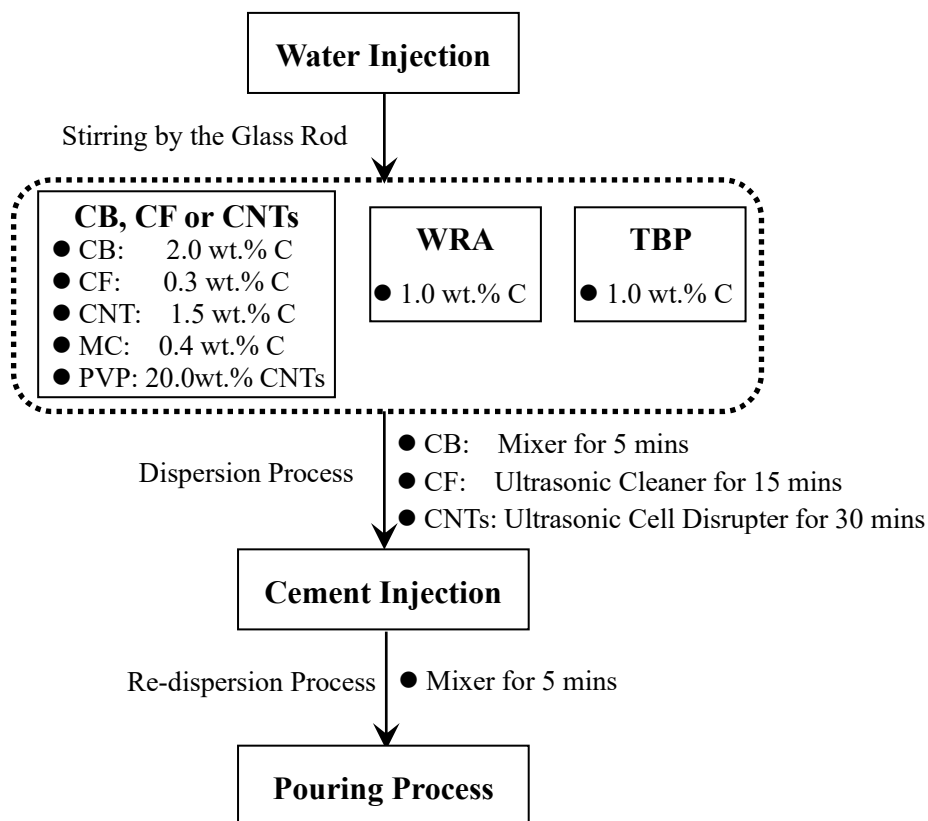
The anode system is a critical component for the ICCP of RC structures because it determines the efficiency of delivering the polarizing current to the protected steel bars [17]. Currently, various anode materials have been investigated [18-22], e.g., titanium, zinc, conductive polymers, conductive paint, coke breeze asphalt, etc. However, these anode systems generally suffer from poor durability, or are expensive [23], and have poor compatibility with concrete, severely degrading the delivery efficiency of the ICCP electric field. In recent years, cement conductive composites have been widely investigated as an anode layer of ICCP systems for RC structures due to their excellent durability, outstanding compatibility with concrete materials and convenience of installation [24].

However, most previous studies have focused on the preparation of cement conductive anodes [25-31], and few of them have paid attention to the serviceability and durability of the anodes and how their anodic functionality is lost in ICCP systems. As is well known, the service life of an ICCP system is primarily determined by that of the anode used [32], so it is very important to reveal the causes of the ageing behavior in the ICCP system for RC structures and to predict the service life of the cement conductive anode. Therefore, a galvanostatic polarization experimental method is implemented in this study to evaluate the serviceability of cement conductive anode for the ICCP system of RC structures. Additionally, the long-term performance of a carbon-enhanced cement conductive anode is discussed.

## **2. EXPERIMENTAL PROCEDURE**

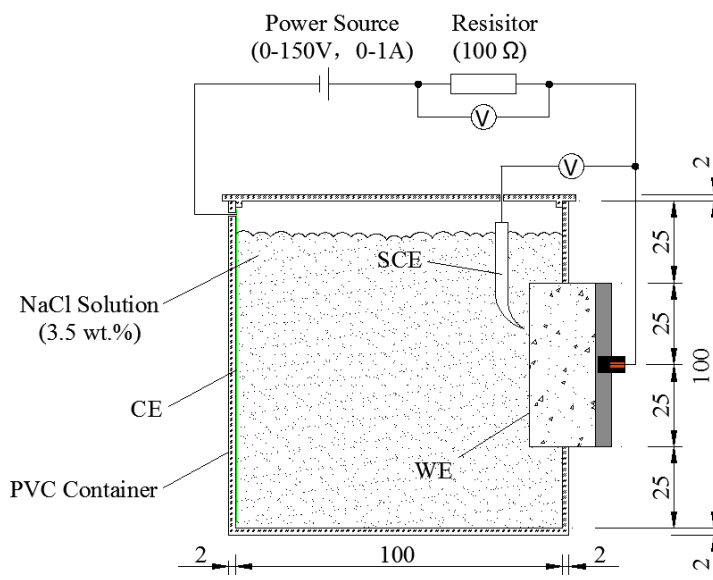
### *2.1 Galvanostatic polarization test*

In general, conductive fillers are required for preparing cement conductive anodes. Among them, carbon materials are commonly used as conductive fillers [23-25, 27, 28, 33], such as graphite powder, carbon fibre (CF), carbon nanotubes (CNTs), etc. In this study, a multiscale carbon-enhanced cement anode was adopted to investigate the serviceability and durability of cement conductive anode. CF, CNTs and carbon black (CB) were used as the conductive admixtures added into the cement paste, and the specific preparation process is shown in Figure. 1, which has been reported in our previous study [24], and the details are not given here.

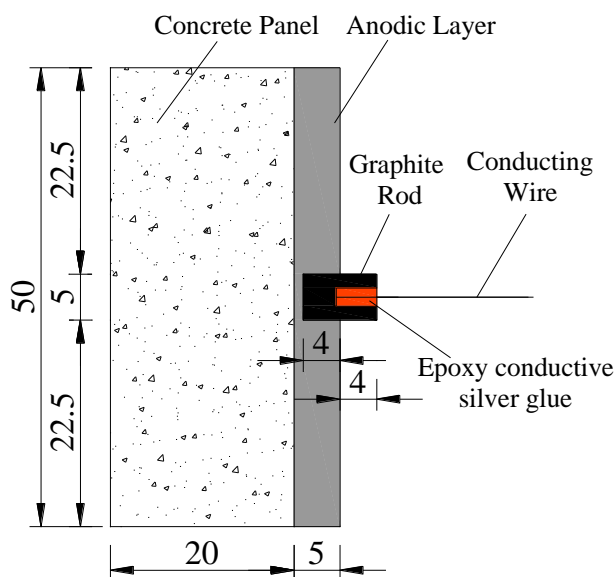


**Figure 1.** Preparation process of multiscale carbon-enhanced cement anode [24].

A galvanostatic polarization test was adopted to investigate the serviceability and durability of the cement conductive anode, which was conducted in a classic three-electrode system, as shown in Figure 2. A stainless-steel mesh and a saturated calomel electrode (SCE) were used as the counter electrode (CE) and the reference electrode (RE), respectively, and NaCl (3.5 wt. %) solution was adopted as the electrolyte solution. To be closer to a cement conductive anode layer that would be used in a practical engineering project, the work electrode (WE) consisted of a concrete panel and a cement conductive anode layer. The concrete panel (50×50×20 mm<sup>3</sup>) was cut from a C30 concrete specimen (100×100×100 mm<sup>3</sup>). Then, the conductive cement anode layer with a thickness of 5 mm was deposited onto the concrete panel, and a graphite rod (Φ 5 mm×8 mm) was embedded into the centre to act as the primary anode. After 24 hours in airtight conditions, the specimens were demolded. A conductive wire was secured in the hole located in the centre of the graphite rod using epoxy conductive silver glue. The structures of the WE are shown in Figure 3. Five WE samples were prepared. After 3 d of accelerated curing in a heated water bath (60 °C), the WE samples were fixed in the centre of the sides of PVC containers, and the interfaces between the samples and PVC were sealed by epoxy resin to avoid the outflow of the electrolyte solution.



**Figure 2.** Schematic of the long-term polarization experimental setup used (unit: mm).



**Figure 3.** Structures of the work electrode (unit: mm).

To investigate the influence of different degrees of chloride attack in concrete on the serviceability of the cement conductive anode, three WEs were immersed into electrolyte solution (3.5% NaCl solution) for different times prior to the galvanostatic polarization test. The sample with an immersion time of 28 d was recorded as WE #1; another two with an immersion time of 7 d were recorded as WEs #2 and #3. The control sample that was not unpolarized was recorded as WE #0. To shorten the test period, a constant high current density of  $20 \text{ A/m}^2$  versus the outer surface area of the anode was applied. Additionally, the voltage between the two ends of a standard  $100\text{-}\Omega$  resistor

connected to the WE in series was measured periodically, which could monitor the circuit current. The WE polarization potential versus the SCE was measured periodically by a high impedance voltmeter. To reduce the influence of the change in the pH value and the ionic concentration of the electrolyte solution on the test results, the solution was replenished every 24 hours. When a primary anode exhibited signs of shedding during the galvanostatic polarization process caused by the damage of the interface between the cement conductive anode and the primary anode, we repaired it using the same fresh cement conductive anode. After 3 d of accelerated curing of the WEs in a heated water bath (60 °C), the test continued.

## 2.2 SEM and XRD measurement

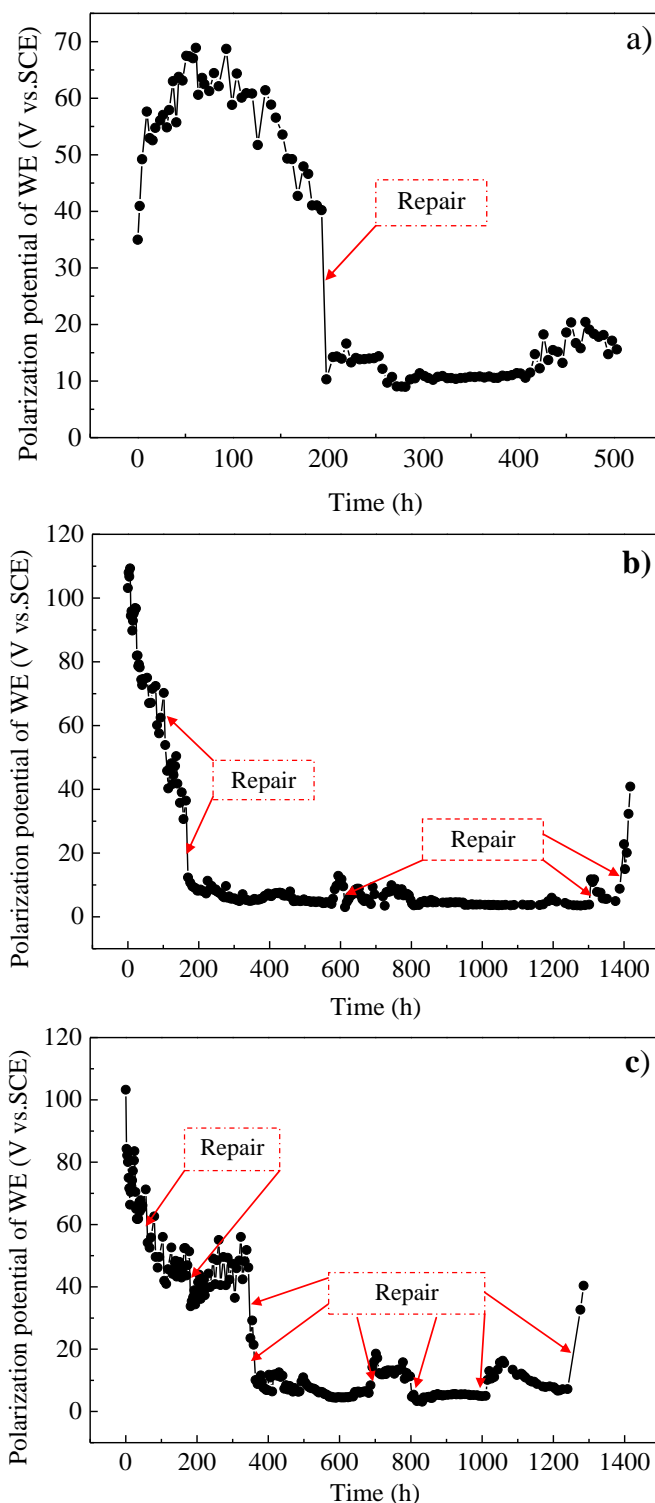
At the end of the accelerated polarization experiment, all of the samples including the polarized and unpolarized cement conductive anodes were chipped into small blocks and ground into powders with a maximum particle size of less than 2  $\mu\text{m}$ . The small blocks were used to observe the surface morphology of the CFs by scanning electron microscopy (SEM), and the powders were used to analyse the phase composition of the anodes via X-ray diffraction (XRD).

## 3. RESULTS AND DISCUSSION

### 3.1 Serviceability of the cement conductive anode

The change in the anodic polarization potential versus time is shown in Figure 4. Because the immersion time in NaCl (3.5 wt. %) solution for the concrete panel of WE #1 is 28 d and that of WEs #2 and #3 is only 7 d before the polarization tests, more free ions (i.e.,  $\text{Na}^+$ ,  $\text{Cl}^-$ ) and water diffuse into the concrete panel of WE #1, which causes the circuit resistance of WE #1 is to be less than those of WEs #2 or #3. Thus, the initial potential of WE #1 is less than that of the other two WEs, as shown in Figure 3. At the beginning of the polarization stage (i.e., from tens to approximately two hundred hours for WE #1 and #2, and from tens to approximately four hundred hours for the WE #3), a large number of free ions (e.g.,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{OH}^-$ ) in the concrete panel of WE #1 can produce an anti-electric field, resulting in an increase in the polarization potential. Conversely, the contents of the free ions in the concrete panels of WEs #2 and #3 are very low, so the anti-electric fields in the two WEs are small and have little influence on the potential; however, a substantial increase in the water content in the concrete panels reduces the circuit resistance, causing a decrease in the potential of WEs #2 and #3. These results show that the resistance of the concrete panel has a significant influence on the polarization potential, and this agrees well with the results reported by Xu et al. [23] and Hassanein et al. [15] that the concrete resistivity has a marked influence on the electric field distribution of an ICCP system in an RC structure.

During the middle time period of the galvanostatic polarization process, the potential of all the WEs is at a steady state, indicating that the resistances of the WEs, including the concrete panel and the cement anode, are stable.

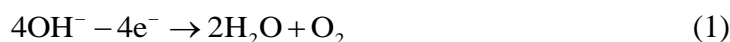


**Figure 4.** Potentials of the WEs when applying  $20\text{-A/m}^2$  galvanostatic polarization. a), b) and c) are the anodic polarization potentials of WEs 1#, 2# and 3#, respectively.

To compare with the specimens that thoroughly lost the serviceability, the polarization test of WE #1 was stopped, and thus, the polarization time of WE #1 was 503 hours. Shown in Figures 4 b) and c), the potential of WEs #2 and #3 increases significantly in the later period of the polarization process. This shows that the conductivity of the WEs begins to degrade, and its conductivity is determined by the

anode layer at this time, so the conductivity of the cement anode is declining. This means that the efficiency of the ICCP system in a practical engineering case will be reduced if the cement anode continues to service when its conductivity begins to significantly reduce.

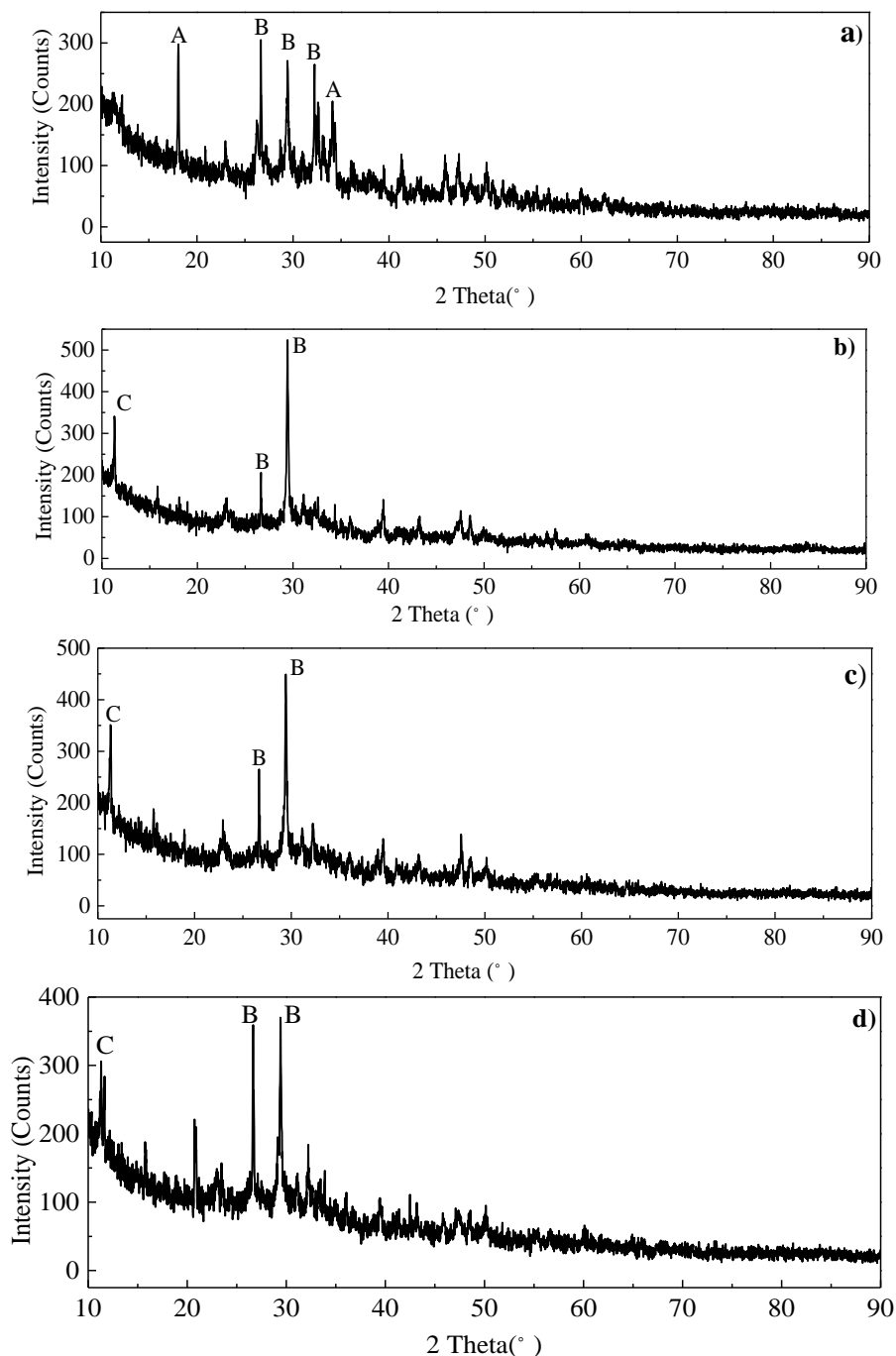
The mineral compositions of the unpolarized cement anode of sample #0 and the polarized cement anode of samples #1, #2 and #3 were determined by XRD analysis. The results are shown in Figure 5. The primary crystalline phases of the unpolarized sample are shown to be CH and C-S-H while those of the polarized samples are shown to be C-S-H and Friedel's salt ( $C_3A \cdot CaCl_2 \cdot 10H_2O$ ) and no CH phase is found. Ettringite is not detected in the XRD patterns in these two cases, which may be because its content is too low. During the polarization process of the cement conductive anode, chloride ions are forced to migrate into the cement anode, and then, the following anodic reactions occur around the conductive admixtures in the cement matrices:



These reactions can reduce the pH value near the conductive fillers, which causes calcium hydroxide crystals in the cement matrices to dissolve [29, 30]. Accordingly, calcium hydroxide crystals are absent in the polarized cement conductive anodes. Meanwhile, the cement hydration products containing aluminium (i.e.,  $C_3A$ ,  $C_4AF$ ) tend to adsorb some chloride ions, forming Friedel's salt, which is shown in the associated XRD results of Figures 4 b), c) and d). The formation of Friedel's salt diminishes the porosity of the cement anode and slows the transport of ions [34], which reduces the conductivity of the cement composite. However, Friedel's salt has already formed and calcium hydroxide crystals have already been reacted in sample #1 with more serious chloride attack, but its polarization potential has little change, and thus, the formation of Friedel's salt and the reaction of calcium hydroxide crystals have little influence on the anodic function.

Because the surface morphologies of CNTs and CB in cement matrices cannot be observed clearly by SEM, we only analysed the surface morphologies of CF. The resulting SEM images clearly show that the surface of the majority of CFs in the polarized samples is rougher than that of the unpolarized samples. Figure 5 a), b), c) and d) present the SEM images of CF in samples #0, #1, #2 and #3, respectively. The surface of the CF in samples #2 and #3 is shown to be much coarser than that of samples #1 and #0; additionally, that of sample #1 is shown to be coarser than that of sample #0. Similar results are also reported by Xu et al. [23] and Anwar et al. [28]. With such high current density polarization, active site atoms on the carbon material surface are easily oxidized to form oxygen-containing surface groups such as C-OH, C=O, COOH and even probably  $CO_2$  [35]. Consequently, the surface of CFs in the polarized samples becomes coarser than that of the unpolarized samples. The extent to which the carbon materials surface is coarse should be proportional to the Coulombs per gram (C/g) of the CF (which is called the extent of electrochemical oxidation) during the process of electrochemical oxidation. Therefore, the loss of the anodic function of the cement conductive anode is primarily caused by the electrochemical oxidation of the conductive admixtures; the life expectancy of the cement conductive anode is primarily determined by the extent of electrochemical oxidation of the carbon materials when the conductivity begins to seriously degrade. The content of carbon admixtures is greater, which means that the service life of carbon-based cement composites is longer, but the workability and mechanical properties of the cement paste may become worse [36]. Therefore, the content of carbon

admixtures should be as high as possible when preparing a conductive cement anode only if it can meet the requirements of the constructability.

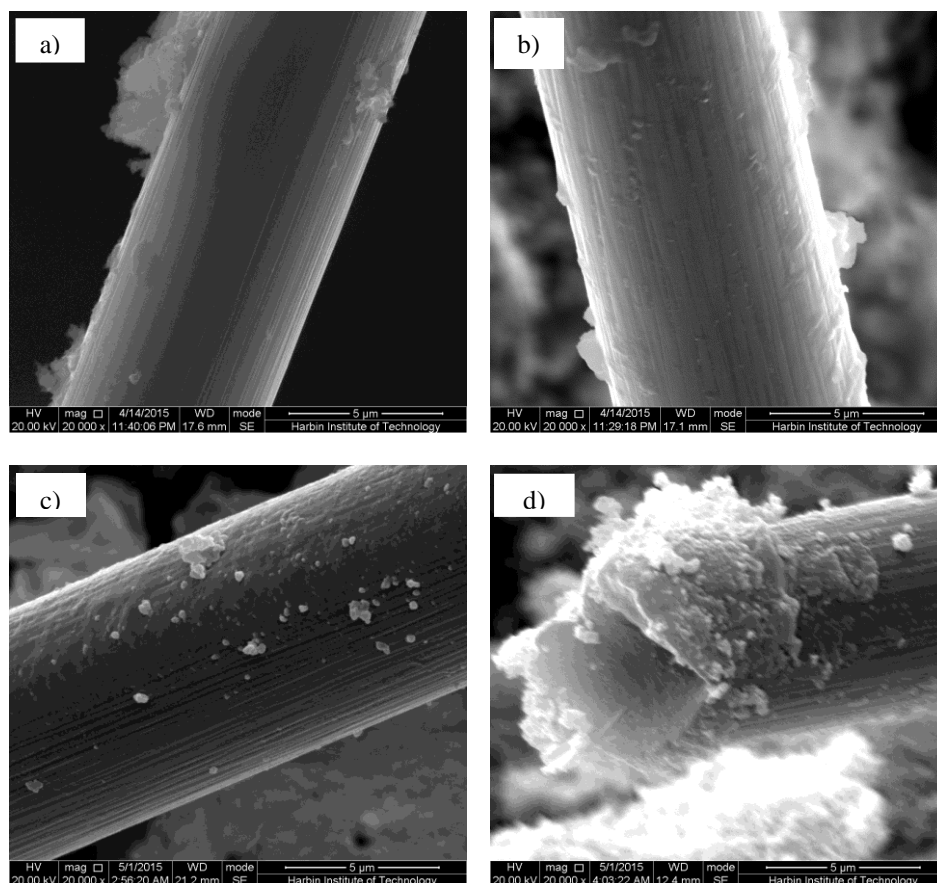


**Figure 5.** XRD patterns (A, B and C denote Ca(OH)<sub>2</sub>, C-S-H, C<sub>3</sub>A·CaCl<sub>2</sub>·10H<sub>2</sub>O, respectively). a), b), c) and d) are the XRD patterns of 0#, 1#, 2# and 3#, respectively)

Because the anodic reactions (such as oxygen and chlorine evolution) occur around the conductive fillers in the cementitious matrices, rather than in the interface between the cement-based anode and concrete panel, the interface in all the WEs is found to be good at the end of the galvanostatic



polarization test. This also confirms that the cement conductive anode does has a better compatibility with concrete than the metal anode.



**Figure 6.** SEM images of the CF in samples a) #0, b) #1, c) #2, and d) #3.

### 3.2 Repair of the interface between primary anode and cement anode

Some jumps of the polarizing potential are found in Figure 4, which are just caused by the repair of the interface. The potential of the primary anode is the highest in the system, and a large number of anions are driven to move around the primary anode, which damages the interface between primary anode and cement conductive anode. Anwar et al. [28] found that the rise in the amount of some elements, such as Si, K, Na and Ca, should be the primary reason for the damage in the interface between the primary anode and the cement conductive anode in the galvanostatic test. In the study by Hu et al. [37], a more porous microstructure and severe propagation of cracks could be observed near the primary anode in the galvanostatic test with a higher current density. Therefore, when the primary anode tends to drop from the cement conductive anode, the interface can be artificially repaired.

Early in the polarization process, the polarization potential exhibited a drop after the repair, which shows that the repair can substantially improve the efficiency of the ICCP current delivery onto the protected steel bar. However, when the conductive admixtures in the cement matrix are thoroughly

deteriorated, the polarization potential does not decrease after the repair at the latter period of the polarization process, which indicates that the repair at this moment is ineffective.

### 3.3 Life expectancy of carbon-based cement conductive anodes

Since the life expectancy of the cement conductive anode is primarily determined by the extent of electrochemical oxidation of the carbon admixtures when the conductivity of the cement anode starts to degrade, the life expectancy of the cement conductive anode layer in practical engineering can be calculated using the following equation:

$$T = \frac{t \cdot i \cdot D}{I \cdot d} \quad (3)$$

where  $T$  denotes the life expectancy of the anode layer in the ICCP system for a practical RC structure;  $D$  and  $d$  denote the thickness of the anode layer in a practical ICCP system and galvanostatic polarization test, respectively;  $I$  and  $i$  denote the current density in the practical ICCP system and the galvanostatic polarization test, respectively;  $t$  denotes the polarization time when the conductivity of the cement conductive anode begins to seriously degrade under the galvanostatic polarization test.

It should be noted that the life expectancy  $T$  is proportional to  $D/d$ .  $D/d$  in Equation (3) represents the ratio of the contents of conductive fillers per unit area in the anodes between practical ICCP system and galvanostatic polarization test. For example, assume that the multiscale carbon admixture-enhanced cement anode presented in this study is applied in practical engineering and the thickness of the anode layer in the practical ICCP system is 5 mm. From the above test, we know that  $t$  is approximately 1240 hours and  $i$  is 20 A/m<sup>2</sup>. If a current density of 30 mA/m<sup>2</sup> (versus the anode area) is adopted in a practical ICCP system, the life expectancy of multiscale carbon admixture-enhanced cement anode should be approximately 94 years, and this result highlights the significant superiority of the cement conductive anode in terms of durability.

## 4 CONCLUSIONS

This paper investigates the long-term performance of a cement conductive anode for an ICCP system and presents the reasons for the loss of its anodic function. The influence of the concrete panel on the polarization potential shows that the resistance of concrete has a strong relationship with the delivered impressed current of the ICCP system for protected RC structures. Friedel's salt tends to form, and calcium hydroxide crystals tend to react in the cementitious conductive anode with the long-term operation of the ICCP system, but the presence of both of these cases have little influence on the serviceability of the cement conductive anode.

The conductivity of the conductive admixtures added into cement anode directly determines the anode's serviceability, and thus, the life expectancy of the cement conductive anode is primarily dependent on the extent of electrochemical oxidation. The content of the conductive admixtures is higher, which means that the service life of the cement anode layer is longer in practical engineering applications only if it can meet the requirements of the constructability. Additionally, the interface

between the cement anode and concrete is found to not be easily damaged since anodic reactions only occur around the conductive fillers in cementitious matrices, which is not the case for common metal anodes. The repair of the interface between the primary anode and cement conductive anode can substantially improve the efficiency of the ICCP current delivery to the steel bar before the cement conductive anode loses its anodic function. Moreover, considering that the life expectancy of the cement conductive anode is primarily determined by the extent of the electrochemical oxidation of the carbon admixtures, it can be predicted that the life expectancy of the multiscale carbon-enhanced cement anode studied in this paper is approximately 94 years.

#### DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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