

Short Communication

Electrochemical Investigation of the Solid-State Reference Electrode Based on Activate Carbon for Corrosion Monitoring of Reinforced Concrete Structures

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The electrochemical activated carbon is a kind of application for assembling the solid-state reference electrode. The electrochemical characters of the reference electrode are temperature response, potential stability and the impact of classic ions, which are surveyed at length. The performance of polarization is confirmed as well. Moreover, the electrochemical impedance spectroscopy of the reference electrode is examined. In the corrosion monitor of reinforced concrete structures, the conclusion gives the baseline to apply the electrode.

Keywords: Corrosion monitoring; Reinforced concrete; Activate carbon; Polarization; Electrochemical impedance spectroscopy

1. INTRODUCTION

In building structures, concretes with reinforced steel are generally applied, which are called reinforced concretes (RC). In reinforced concretes, the structure of the steel is of enhanced stability and excellent tensile strength. However, in the concrete structures, corrosion of rebar makes the useful life declined. In the past few decades, this problem has taken up surprising rates, causing large amount of costs for repair. Sometimes, the cost outweighs the initial construction cost, and in some extreme cases, finally causing the structural collapse. Commonly, by the high alkalinity ($\text{pH} > 13.5$) of the pore solution, concrete can protect the reinforced steel from corroding. Steel, with high alkalinity, keeps passivated. When a large number of chloride ions have been through the reinforcement, or because of the carbonation, the pH value of the pore solution is lower. The reinforced steel is of depassivation [1-3], and the protective film is broken down. Therefore, in terms of the structural stability, the

monitoring rebar corrosion provides important information and assistants to rehabilitate and remedy the concrete structures. Some most common techniques for monitoring or measuring the electrochemical corrosion are electrochemical impedance spectroscopy (EIS) [4], linear polarization resistance (LPR), and measurement of half-cell potential (E_{corr}). In the measurement of the corrosion rate, these techniques are necessarily demand of reference electrodes/sensors. In the measurement of half-cell potential, in regard to the external reference electrodes, the steel rebar potential was tested. However, for surface mounted techniques, these external reference electrodes are accompanied by some certain limitations. For instance the reference electrode leaks liquid, which pollutes the measurement system and gives unstable signals due to the resistance from the structure of concrete. [5-7].

Therefore, on account of the typical three-electrode system, the key element to establish the electrochemical corrosion sensors is the solid-state and embeddable reference electrode. The common liquid reference electrodes include the copper/copper sulfate reference electrode (CSE), the saturated calomel electrode (SCE) and the standard hydrogen electrode (SHE), etc. In most conditions, these liquid reference electrodes, due to their reliable performance, are generally adopted to the most laboratory experiments. However, the weak structure and the short lifespan decide that, in the field, these reference electrodes cannot be adopted. For examples, for various applications, Michalska and Guth et al. recently inspected some features and designs of SSRE [8, 9]. In the studies of electrochemistry, an optimal electrode should be zero current potentiometry and non-polarizable. Such electrode can not pollute the sample, and the system must have long useful life [10]. European Federation of Corrosion (EFC) has checked the features of embeddable reference electrodes and electrochemistry for concrete. EFC announced that the service status has four types of classic embeddable reference electrodes that are lead, graphite, Ag/AgCl/KCl and MnO_2 , which, tens of years ago, have been used in Gimsøystraumen Bridge of Norway [11]. On the basis of the field experience of European Federation of Corrosion, the success rate of reference electrode installation is in the low level. Hence, for the monitor of RC structural corrosion, it is looking forward to studying the cutting-edge functional material to set up the embeddable and solid-state reference electrode.

In concrete, faced with invasive ions such as chloride and hydroxide, carbon material is famous for its inert behavior[12, 13]. When at elevated temperature the material is activated (commonly above 700 °C), the material turns into highly porous, which is called activated carbon as well [14]. On account of its higher surface area, when soaked in an electrolyte, the activated carbon electrode becomes a large electrical double layer capacitance ($\text{EDLC} > 50 \text{ F/g}$) [15]. Therefore, for super capacitors, the activated carbon electrodes are generally regarded as a kind of electrode material [16]. The most surface proportion of an activated carbon electrode is from its micro and nano-porosity. The large electrical double layer capacitance can be employed to the stabilization of the potential of activated carbon electrode in high ionic electrolytes. At the present work, activated carbon electrode was regarded as solid state reference electrodes, whose reversibility features and stability of potential were examined electrochemically in high alkaline passive (without chloride) and active (with chloride) solution medium. The study compares the results with traditional saturated calomel electrode and conducts the corrosion evaluation of steel rebar as well.

2. EXPERIMENTS

2.1. Preparation of activated carbon and activated carbon electrode

This study used palm date seed as the precursor for activated carbon productions and hydrochar, and got the seed in the local horticulture shop in Zhenzhou, China. The study used normal water to wash the whole raw palm date seed material several times, and then, used the distilled water to remove flesh and dirt. At room temperature, the samples were dried, and a grinder was used to crush the samples to get 1–2 mm particle sizes. There was an automatic stainless-steel reactor with water capacity (10L) that were made for hydrothermal carbonization. Precisely, 1 kg of the palm date seed sample was turned into the hydrothermal reactor. Distilled water (5L) was added to safeguard that the sample was totally soaked. At 5 °C/min heating rate, the reactor was sealed and heated to 200 °C for 10 h, after which, at room temperature, the reactor cooled down. From the reactor, the brownish hydrochar was got and played the role of a solid residue. Distilled water was used to wash the recovered product a few times and was put into an oven at 105 °C to heat for 24 h. After which, at ratios of 1:1, the hydrochar was mixed with NaOH, hydrochar:NaOH (w/w) and was stored one night, then dried by the oven at 105 °C for 24 h. At the temperature of 600 °C and under a consecutive nitrogen (N₂, 99.995%) for 1 h, an automatic electric vertical furnace would activate the NaOH-pretreated hydrochar. As the furnace cooled down to room temperature, the collection of produced activated carbon was done, and the furnace decreased the pH value of the washing solution from 6 to 7 by repetitively rinsing with hot distilled water. In the end, the oven dried the wet activated carbon at 105 °C for 24 h, and the dry activated carbon was kept in an airproof container for further use.

The graphite/carbon paste played the role of adhesion. The mixture of the prepared activated carbon and the commercial graphite/carbon paste was gone through hot pressing. Next, followed by the immersion into water for 24 h, at room temperature the activated carbon electrode is dried for 24 h. At last, the trapped oxygen is removed by applying the N₂ purging.

In order to evaluate the performance of the activated carbon electrode, it was put interior of the concrete a concrete sample. And a mortar sample is adopted to realize the simplicity and to get the proof of concept. By using ordinary Portland cement 42.5, the preparation of the sample was finished. The ratio of sand to cement was 3. And 0.5 % naphthalene-based superplasticizer was mixed. The water to cement ratio of 0.5 was applied to make mortar samples. There was a steel rebar with diameter of 8 mm and 130 mm in length that were put inside of the concrete. In the course of casting, the activated carbon electrode is soaked in the concrete sample.

2.2. Electrochemical measurements

Through the studies including polarization, reversibility and impedance behavior in three electrode cell configuration, the electrochemical behavior was checked. In the study, fabricated activated carbon electrode plays the role of working electrode, platinum foil serves as counter electrode and SCE work as reference electrode. By cyclic polarization method, the investigation of reversibility of activated carbon electrode was conducted, in the potential range of ±20 mV from the

open circuit potential with sweep rate of 1 mV/s. As above, a similar procedure, for polarization test, was adopted. And from the open circuit potential, the potentiodynamic condition with sweep rate of 1 mV/s corresponds to ± 200 mV. For chloride ion exposure experiment, the sample was partially immersed into a 1~3% NaCl solution. For pH sensitivity experiment, the sample was placed at different pH (11-13) medium. The influence of the different medium using different electrode was studied by immersing the sample into different medium for 30 days before record the polarization curve.

2.3. Characterizations

The morphology of activated carbon was characterized by a scanning electron microscope (SEM, Quanta 200, FEI Coropration, Holland). A FTIR (Perkin-Elmer Spectrum One) was used for analysing the surface functional groups of the prepared sample.

3. RESULTS AND DISCUSSION

Fig. 1A and Fig. B illustrates the SEM images of activated carbon at 1000 \times and 3000 \times magnification, respectively. On the activated carbon surface, some porosity was developed by the hydrothermal carbonization process. However, the pores that came into being were constricted and narrow.

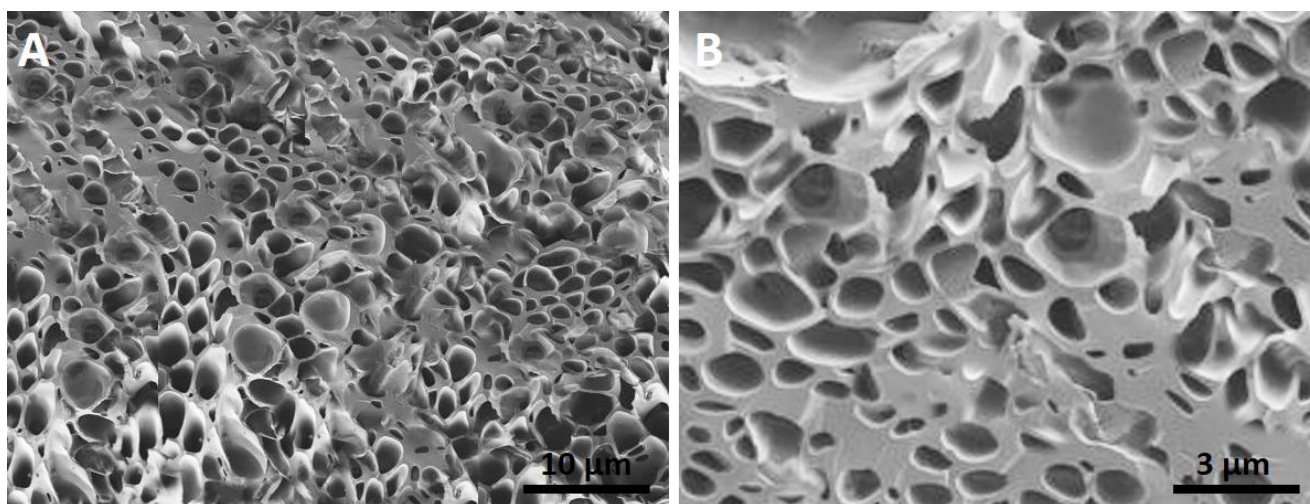


Figure 1. SEM images of activated carbon at (A) 1000 \times and (B)3000 \times magnifications.

Due to subsequent release of volatile organic substances and depolymerization from carbonization, on the hydrochar surface, the pores of different shapes and sizes were found [17]. In the course of hydrothermal carbonization, the pore does not develop largely due to the recondensation of volatile substances. But the hydrothermal carbonization had an essential impact of the cellulose,

hemicellulose, and the sample cell wall's lignin components, which changes the surface properties of the adsorbents. The changes of surface chemistry of the sample may help to transmit the NaOH molecules to the inside of the hydrochar and make plenty of pores [18]. In addition, when communicating with lignocellulosic biomass, NaOH plays the role of reducing agent. As NaOH is at high temperatures, followed by the rest of the hemicelluloses, it first depletes the hemicelluloses; the lignins and celluloses are degraded as well, then, the left NaOH leave the occupied voids of the cell cavities [19]. In terms of undecomposed lignin, its left structures would create different shapes, and on the activated carbon surface, the shapes are with large to medium apertures.

In Fig. 2, FTIR spectra for the palm date seed and activated carbon are demonstrated. From Fig.2, it can be seen that compared with raw material spectrum, the activated carbon spectrum showed less absorption bands, chiefly between 3000 and 1690 cm^{-1} , which showed that after the carbonization, some functional groups that presented in the palm date seed faded away. It is common that the broad bands of both spectra are around 3500 cm^{-1} , which can be contributed to O–H stretching vibration. The band at *c.a.* 2900 cm^{-1} is due to C–H stretching vibration and is found solely in raw material spectrum, which indicates that during the achievement process of activated carbon, hydrogen was largely eliminated [20-23]. In palm date seed spectrum, the bands at 1740 and 1600 cm^{-1} can be put down to C=O stretching vibrations in alkenes groups and carboxyl as well as aromatic rings. Generally, the bands of both materials are at 1600 cm^{-1} . The bands 1500 and 1400 cm^{-1} are ascribed to C–C stretching [24]. In addition, the bands between 1260 and 1050 cm^{-1} can be assigned of C–O stretching in esters, carboxyl acids, phenols and alcohols [25]. Commonly, the bands of activated carbon and raw material are at 1050 cm^{-1} . Due to the out-of-plane angular deformations of aromatic rings, the bands are at *c.a.* 600 cm^{-1} [26]. In activated carbon spectrum, the bands around 3500 and 1000 cm^{-1} were attenuated while the intensity of band at *c.a.* 600 cm^{-1} boosted, which proved that there was a change in the performance of the raw material [27].

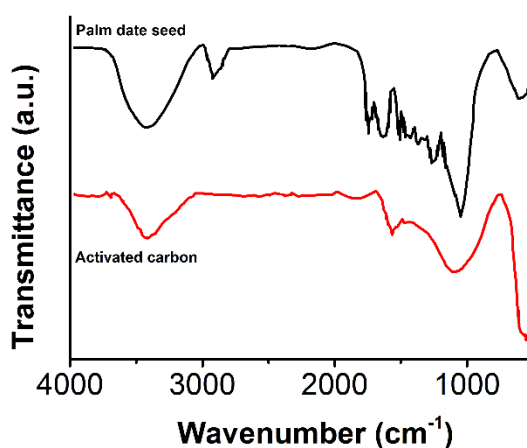


Figure 2. FTIR spectra of palm date seed and synthesized activated carbon.

In different kinds of alkaline media with pH = 11, 12 and 13, in the fabricated activated carbon electrode, its potential stability of was inspected. Fig. 3A presents the potentiometric reaction of the

fabricated activated carbon electrode in three various types of alkaline media, which initially was examined for one month. During the measured period, there was a potential of -219 mV that was at lowest and a highest potential of -234 mV vs SCE. In each test solutions, in the average potential was discovered to be -228 mV vs SCE. This result shows in alkaline medium, the potential reliability of activated carbon electrode.

As shown in Fig. 3, pH 12 media with 1–3% of NaCl was used to study the interference influence of chloride ion. In active chloride medium, the potential was about -231 mV in regard to SCE, and during the whole the immersion period, from the observation, the potential was stable, whose variation in active and passive medium is between 23 mV. From the results, the conclusion can be made that quantity of chloride ions has no impact on the potential of the fabricated activated carbon electrode. The study shows that in chloride contaminated solution, the reliability of the fabricated reference electrode is good. It is very essential for high chloride polluted real field corrosive environment monitoring.

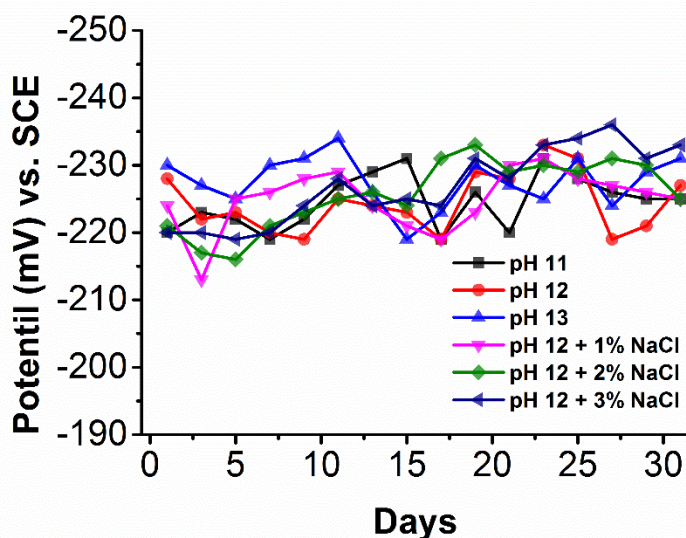


Figure 3. Potential stability of fabricated activated carbon electrode in different alkaline medium and in pH 12 medium with 1%, 2% and 3% NaCl.

Optimally, the reference electrode is not polarizable, during the measuring time, which gives stable potential. In the current study, from the open circuit potential to 200 mV in regard to SCE, polarization method was used to test the stability of activated carbon electrode. The common polarization curve of activated carbon electrode can be shown in Fig. 4, and the Table 1 indicates the relevant polarization parameters. In the three fabricated reference electrode, the observed polarization current was observed to be very low. For the polarization curve recorded at pH 11, the corrosion current was 0.021 mA/cm^2 . This current slightly increased after pH condition increasing. The corrosion currents were 0.022 and 0.023 mA/cm^2 for the polarization curve recorded at pH 12 and pH 13, respectively. On the other hand, the corrosion potentials showed a constant value, which were -217, -215 and -216 for the polarization curve recorded at pH 11, pH 12 and pH 13, respectively.

During the study, the three various kinds of alkaline solutions, in the course of the measured time, do not alter their polarization current and potential. The study indicates superior repeatability, sensitivity and suitability of the fabricated activated carbon electrode. It also can be seen that the proposed electrode monitoring method showed a similar reliable results compared with other monitoring approach, such as electrochemical frequency modulation [28], electrolyte film [29] and radio frequency identification [30].

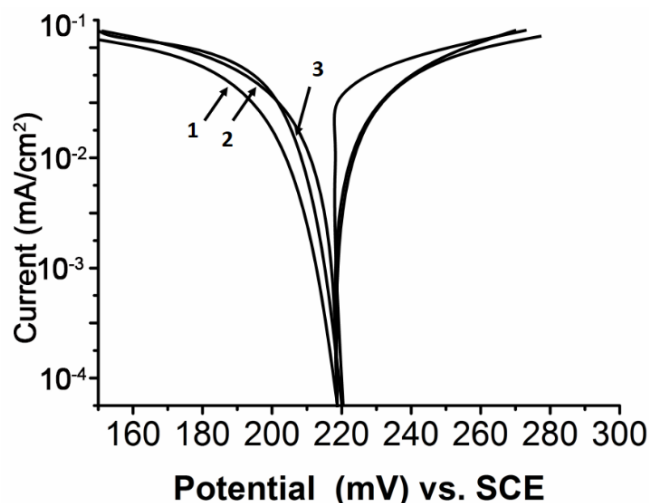


Figure 4. Polarization curve of activated carbon electrode (Condition 1: pH 11; condition 2: pH 12; condition 3: pH 13; scan rate: 1 mV/s).

Table 1. Polarization parameters of activated carbon electrode in different pH medium.

Activated carbon electrode	I_{corr}	(mV vs SCE)	β_a (mV/dce)	β_c (mV/dce)
1	0.021	-217	197	189
2	0.022	-215	195	202
3	0.023	-216	182	201

After exposing for 30 days, in concrete like alkaline solution condition, the corrosion evaluation of steel rebar was conducted. In regard to saturated calomel electrode and fabricated activated carbon electrode, the steel rebar was inspected. The Fig. 5 is showing the resulting potentiodynamic polarization curve (relevant polarization parameters were summarized in Table 2). In highly corroded steel, the corrosion potential of rebar was discovered to be -788 mV vs SCE while the corrosion potential of bare rebar was discovered to be -660 mV vs SCE. In regard to the activated carbon electrode, E_{corr} of steel rebar was similarly found at -730 mV and -642 mV. In the negative direction, the increasing corrosion potential shows that when the rebar is in active state, the rebar is akin to SCE. On the other hand, Higher corrosion current density values for steel were noticed in active condition than passive condition. Compare with other electrode [31], the activated carbon could performance a similar reliable result with a much lower material cost. All the studies suggest that

activated carbon electrode may distinguish between the passive and active state of steel rebar. Activated carbon electrode performed very well both in active and passive state of steel in concrete.

Table 2. Polarization parameters of different electrode with different rebar condition in pH 12 medium.

Electrode	I_{corr}	(mV vs SCE)	β_a (mV/dce)	β_c (mV/dce)
Bare + SCE	0.032	-660	205	209
Corroded + SCE	0.057	-788	215	245
Bare + Activated carbon	0.027	-642	202	202
Corroded + Activated carbon	0.042	-730	208	211

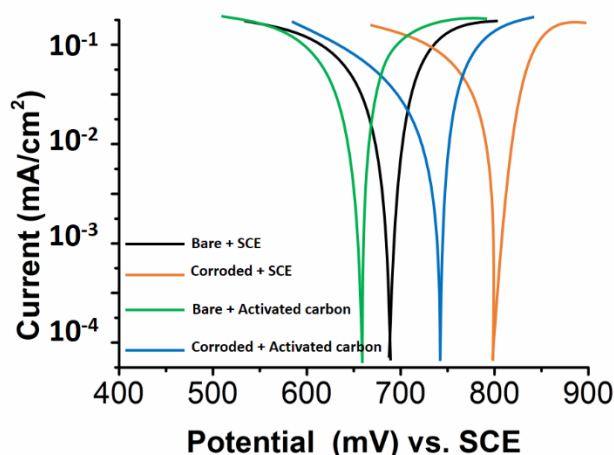


Figure 5. Potentiodynamic polarization studies of bare steel rebar and steel rebar exposed in pH 12 medium with respect SCE and activated carbon electrode. Scan rate: 1 mV/s

In concrete structure, with the purpose of characterizing the activated carbon electrode as embeddable corrosion evaluation reference electrode for in-situ rebar corrosion potential examination, the activated carbon electrode was added into concrete. The casted concrete cube was corrosion, which was induced by 1% NaCl, 2% NaCl and 3% NaCl respectively (relevant polarization parameters were summarized in Table 3). Through the potentiodynamic polarization method, the activated carbon electrode was used as in-situ reference electrode to measure the corrosion potential of steel rebar that was inside of concrete cube. For the purpose of comparison, in regard to SCE as ex-situ reference electrode, steel rebar corrosion potential was examined as well. From the current extend exposure of the concrete. In Fig. 6 indicates the results. When the steel rebar was the initial potentiodynamic polarization studies curve and was put in the active environment of 1%, 2% and 3% NaCl than the comparison with bare, in regard to SCE and activated carbon electrode, the similar tendency of corrosion potential of steel rebar was grew in direction of negative. As the result of corrosion, trend of corrosion potential in direction of negative increased, which presents that the steel rebar converts

passive state into active state. The results illustrate that in concrete structures, the activated carbon electrode is able to distinguish steel rebar of the passive and active state.

Table 3. Polarization parameters of different electrode with different NaCl environments in pH 12 medium.

Electrode	I_{corr}	(mV vs SCE)	β_a (mV/dce)	β_c (mV/dce)
SCE	0.032	-248	205	209
SCE + 1% NaCl	0.044	-322	222	238
SCE + 2% NaCl	0.047	-325	224	239
SCE + 3% NaCl	0.054	-377	233	246
Activated carbon	0.027	-212	202	210
Activated carbon + 1% NaCl	0.031	-249	211	224
Activated carbon + 2% NaCl	0.033	-266	218	229
Activated carbon + 3% NaCl	0.037	-314	223	236

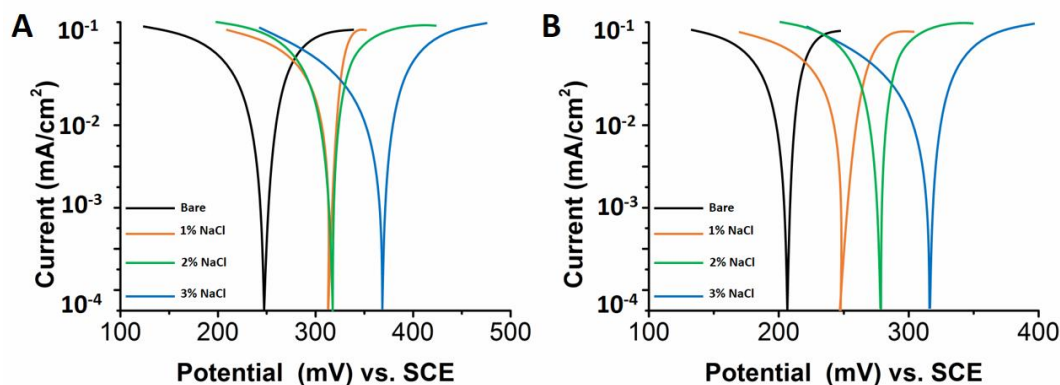


Figure 6. Potentiodynamic polarization curve of steel rebar in mortar with respect (A) SCE and (B) activated carbon electrode at 1% NaCl, 2% NaCl and 3% NaCl. Scan rate: 1 mV/s

4. CONCLUSIONS

From palm date seed, activated carbon with the features of SEM and FTIR, was synthesized. Then, the biosynthesized activated carbon was employed for fabricating solid state reference electrode, which was characteristic with different kinds of pH alkaline condition, no matter the chloride polluted the corrosion monitoring application in concrete or not. The results show that the reference electrode brings reproducible and reliable potentials in terms of SCE. Additionally, in alkaline solution, the corrosion monitoring of steel rebar indicates whether the steel bar is in passive or active states, it can distinguish its status.

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