International Journal of GEOMATE, Feb., 2023, Vol.24, Issue 102, pp.34-41
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2023.102.s8606
Geotechnique, Construction Materials and Environment

ELECTROCHEMICAL EVALUATION OF CORROSION PROTECTION OF REINFORCING STEEL BARS USING SUGARS

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*Corresponding Author, Received: 15 June 2022, Revised: 26 Dec. 2022, Accepted: 28 Jan. 2023

ABSTRACT: This study reports the effect of adding sugars to prevent corrosion of reinforcing bars. The reducing sugars aldose (sugar with an aldehyde group) and, ketose (sugar with a ketone group), and a non-reducing sugar and syrup with an expiration date were used in the experiments. Fehling's reaction, Benedict's reaction, and cyclic voltammetry (CV) tests were performed to investigate the effects of the various sugars on the reductive ability. Because the electrochemical oxidation of sugars requires electrocatalysts, electrodes containing particulate CuO catalysts were used in the experiments. The CV measurements were performed under alkaline conditions to simulate a reinforcing bar in the concrete. The experimental results revealed the influence of different types of sugars on the reductive ability. In Fehling's reaction, fructose was observed to be highly reductive, and its reaction rate was high. In Benedict's reaction, results obtained for waste syrup (WS) were similar to those of fructose, thereby confirming that WS can be used as a reducing sugar. The oxidation onset potentials in the electrochemical experiments were lower for fructose, WS, and glucose, in that order, which was the same as the order of the reaction rates in Benedict's reaction.

Keywords: Corrosion protection, Cyclic voltammetry, Fehling's reaction, Benedict's reaction, sugar

1. INTRODUCTION

Several structures were built during Japan's rapid economic growth period in the 1960s for infrastructure development. The life span of reinforced concrete (RC) structures is generally around 50 years, and many structures currently require inspection and repair. The decrease in the durability of RC structures is primarily owing to corrosion of the reinforcing steel bars [1–5].

Because reinforcing bars are generally located inside concrete, and the pore solution in the concrete is alkaline, a nonconductive film is applied on the surface of the reinforcing bars to prevent corrosion. However, a non-conductive film can be destroyed by the carbonation of concrete and intrusion of chloride ions, and when both water and oxygen reach the film, the steel starts to corrode. As the rebar corrodes, its volume expands by a factor of two or more, and the expansion force destroys the concrete. Additionally, water and oxygen penetrate through cracks and accelerate the corrosion. Controlling corrosion is the key to maintaining the durability of concrete [6–8].

Methods such as using a thicker concrete cover or a lower water–cement ratio have long been employed to control the corrosion of steel bars [9]. A surface impregnating material is also commonly applied to prevent water from penetrating into the steel [10], [11], but it is preferable to omit such laborious methods and use a corrosion-preventive admixture to maintain the durability of a structure.

In recent years, amidst calls for a shift to a recycling-oriented society, reusing waste syrup (WS) has been in focus from the perspective of sustainable development goals and recycling [12–15]. By mixing sugar waste from the food industry into concrete, we aim to not only reuse the waste, but also have the secondary effect of preventing rebar corrosion caused by the reducing performance of sugar. Currently, there is no admixture that increases corrosion resistance; therefore, reducing sugar was selected with the expectation that adding a reducing agent would have a sacrificial anode effect. Electrochemical experiments were conducted to investigate the reducing ability of sugar and its potential use in corrosion protection of rebar.

In this study, we first investigated the reduction performance of WS and other sugars in the Fehling's reaction and Benedict's reaction, and then through cyclic voltammetry (CV) measurements. By comparing the results of these three experiments, the influence of the reduction ability of sugars on the electrochemical properties of rebar was confirmed.

2. RESEARCH SIGNIFICANCE

Waste syrup is food that is normally edible but is thrown away. In our country, syrup is removed from distribution when it becomes discolored or expires. In addition, waste syrup is costly to dispose of and is a burden to companies. This research focuses on the large amount of waste syrup that has reached its expiration date and aims to reuse the resource by utilizing it in the engineering field.

It is investigated that the possibility of extending the time it takes for rebar to rust by utilizing the reducing ability of sugar.

3. MATERIALS AND METHODS

3.1 Materials

The WS used in the experiment was made of glucose-fructose syrup, and its main component was glucose, which constituted about 40% of solid content. The next most abundant component was fructose, which constituted about 30%. Glucose and fructose were also selected as reference substances for comparison [16]. Sucrose, which has no reducing abilities, was also selected as the other substance.

3.2 Fehling's Reaction

As shown in Fig. 1, fructose, and glucose have the same alcohol configuration from the third to sixth carbon positions. These four sugars including sucrose and WS were used in the experiment.

Distilled water was used as the solvent to prepare the reagents and in the experiments. Fehling's solution A was prepared by dissolving 6.92 g of copper (II) sulfate pentahydrate in water to make 100 ml of solution. For Fehling's solution B, 34.6 g of potassium sodium tartrate tetrahydrate and 10.0 g of sodium hydroxide were dissolved in water to make 100 ml of solution [17]. 1 ml each of Fehling's solutions A and B were added into a test tube containing 9 mg of sugar (12 mg in case of WS: The WS contains 75% sugar and 25% water.) to completely dissolve the sugar. The test tubes were covered with Parafilm and heated in a water bath at 80 °C for 1, 2, 3, and 5 min, and then filtered through a filter paper (No. 5C). The filter paper was then dried and quantified.

3.3 Benedict's Reaction

Benedict's solution is a commercially available reagent (Hayashi pure chemical Inc., LTD.) and is sold for clinical testing. Two milliliters of Benedict's solution were added into a test tube containing 9 mg of sugar (12 mg in case of WS). The test tubes were covered with Parafilm and the tube was immersed in water heated to 80 °C for 1, 2, 3, and 5 min. Thereafter, the solution was filtered through the filter paper, which was then dried and weighed.

3.4 Electrochemical Measurements

Electrochemical oxidation of sugars requires electrocatalysts, such as enzymes and metallic catalysts [18–20]. Recently, it has been discovered that metal oxides such as copper oxide (CuO) catalyze the electrochemical oxidation of sugars, especially under alkaline conditions; therefore, a CuO-based catalyst was used in this experiment [21-24].

The CuO-based catalyst was synthesized by heat-treating a carbonate mineral containing Cu [24]. The electrodes used in this study were prepared by casting slurry containing the heated carbonate mineral powders and carbon paste (conductive material) on carbon papers.

D-glucose (aldose), D-fructose (ketose), sucrose (non-reducing sugar), and WS were used to study electrochemical oxidation behaviors of the sugars. The concentration of D-glucose, D-fructose, and sucrose in 0.1 M NaOH solutions was 10 mM. The concentration of WS was also set the same. The composition of the WS was 75% sugars and 25% water. All sugars of WS were assumed to be monosaccharides, and the WS solution was set to have a concentration of 10 mM in 0.1 M NaOH solution.

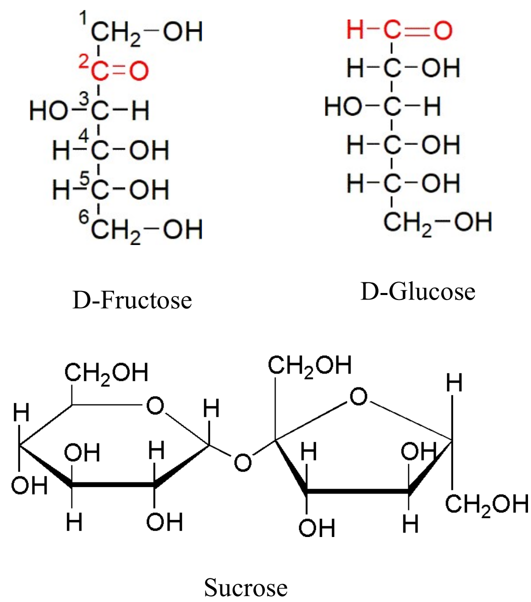

Fig. 1 Molecular structures of sugars.

The CuO electrode was used as the working electrode. A saturated silver-silver chloride electrode (Ag/AgCl) was used as the reference electrode, and a platinum electrode was used as the counter electrode. The measurements were performed in a three-electrode cell with a potentiostat (Hokuto Denko model HZ-7000). A cyclic voltammograms were obtained in the potential ranges of -0.1 to 0.6 V and -0.1 to 0.2 V. In all cases, three cycles with a scan rate of 10 mV s^{-1} were recorded, starting from open-circuit potential in the anodic direction. The electrochemical measurements were performed at 25 °C without stirring.

4. RESULTS AND DISCUSSION

4.1 Fehling's Reaction

The experimental cases are shown in Table 1. The amounts of Cu_2O formed by the reactions of glucose, fructose, sucrose, WS and blank with Fehling's solution were compared (the blanks indicate the case where only distilled water was used as the sample).

Figure 2 shows a photograph of the precipitation obtained through Fehling's reaction after 5 min. As shown in Figs. 2 and 3, Cu_2O was not formed from sucrose. For validation through a blank case, an experiment with only water was also performed, which showed similar results.

Figure 3 shows photographs of the experiment. From left to right: fructose, WS, glucose, sucrose, and blank. After 1 min, a color change began in fructose and WS, followed by a color change in glucose, and after 5 min, fructose, glucose, and WS turned red.

The results of the reaction of Fehling's solution with sugars that exhibited reducing properties are shown in Fig. 4. In the reduction reaction of Fehling's solution, Cu_2O was produced from fructose, glucose, and WS, in that order. Cu_2O was obtained the fastest from fructose, indicating a high reaction rate.

Table 1 Weight of sugars used in the experiment.

Cases	Sugars	Weight of sugar
1	Fructose	9 mg
2	Glucose	9 mg
3	Sucrose	9 mg
4	WS	12 mg
5	Blank	-

4.2 Benedict's Reaction

Figure 5 shows a photograph of the precipitation obtained through Benedict's reaction after 5 min. Fig. 6 shows photographs of color changes in Benedict's solution. From left to right: fructose, WS, glucose, sucrose, and blank. As shown in Figs. 5 and 6, Cu_2O was not formed from sucrose. For validation through a blank case, an experiment with only water was also performed, which showed similar results. Sucrose is a disaccharide consisting of equal amounts of glucose and fructose bound together, commonly known as non-reducing sugar. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose does not reduce Cu^{2+}.

The weights of the precipitates obtained via Benedict's reaction are shown in Fig. 7. Although the results for the reductions using fructose, glucose, and WS were marginally different in Fehling's reaction, there was a marked difference between them in Benedict's reaction. Fehling's solution is a strong alkaline with a pH of 14, whereas Benedict's solution has a pH of approximately 10, which indicates that Benedict's reaction is gradual. Although glucose was easily oxidized in Fehling's solution, Benedict's reaction was slightly slower. This result is similar to that reported by Inoue et al. [16].

Fructose reacted the fastest in Benedict's reaction, similar to Fehling's reaction. In Benedict's reaction, WS and glucose, in that order, yielded Cu_2O.

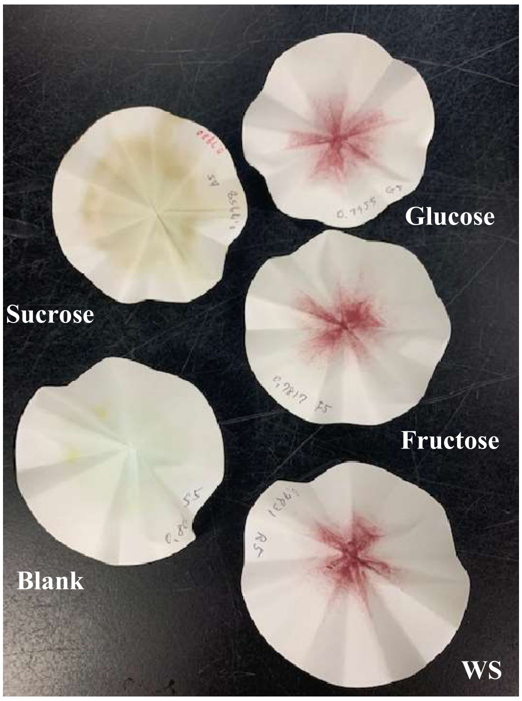

Fig. 2 Photograph of precipitation obtained through Fehling's reactions after 5 min.

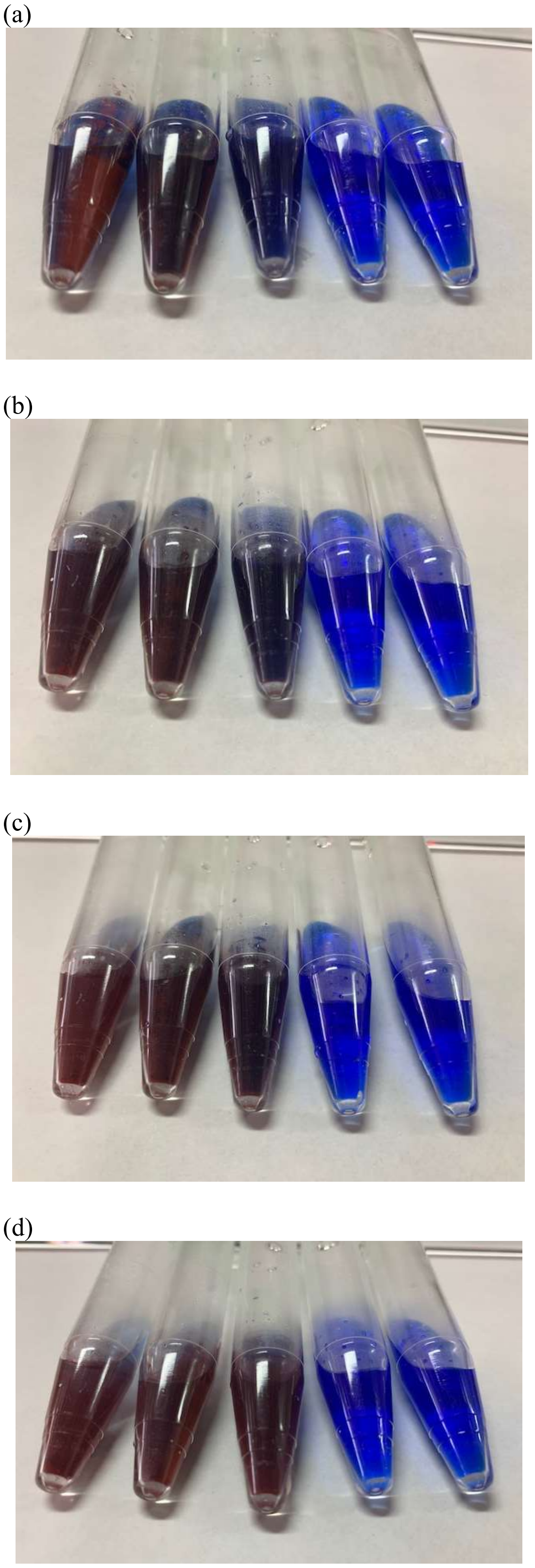

Fig. 3 Color changes in Fehling's reactions from left to right: fructose, WS, glucose, sucrose, and blank (a: after 1 min, b: after 2 min, c: after 3 min, d: after 5 min).

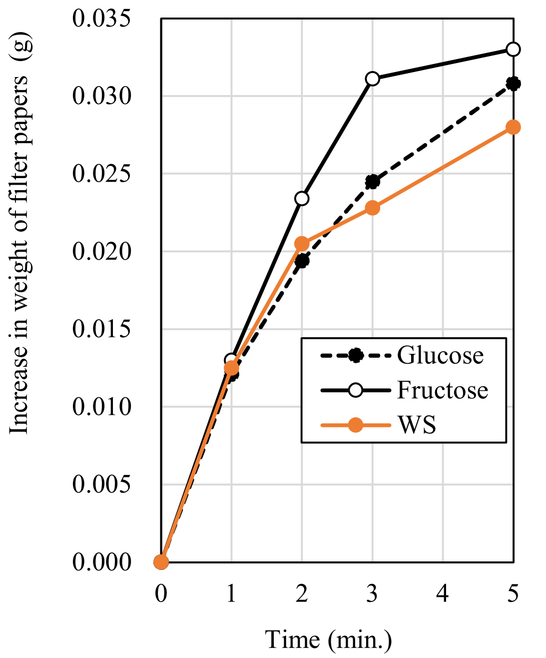

Fig. 4 Increase in the weight of filter papers after Fehling's reactions.

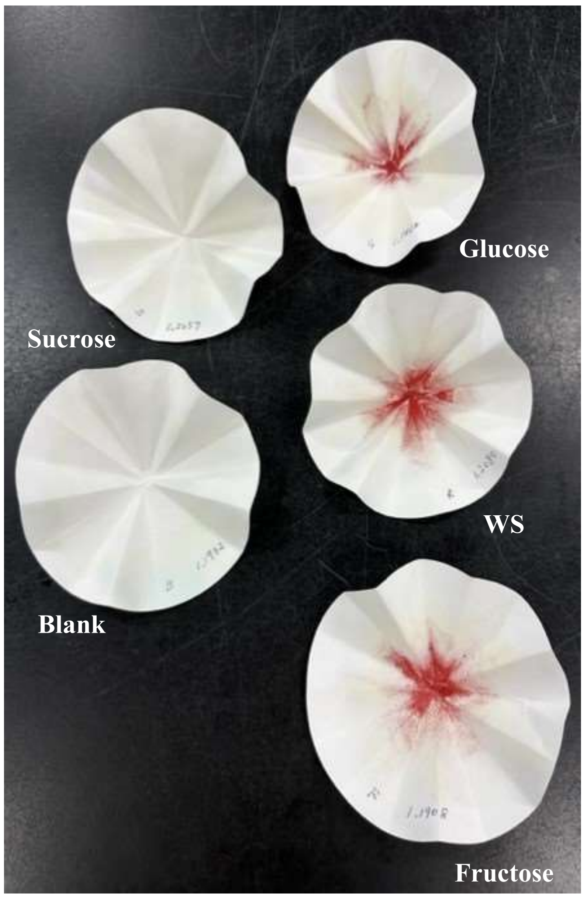

Fig. 5 Photograph of precipitation obtained through Benedict's reactions after 5 min.

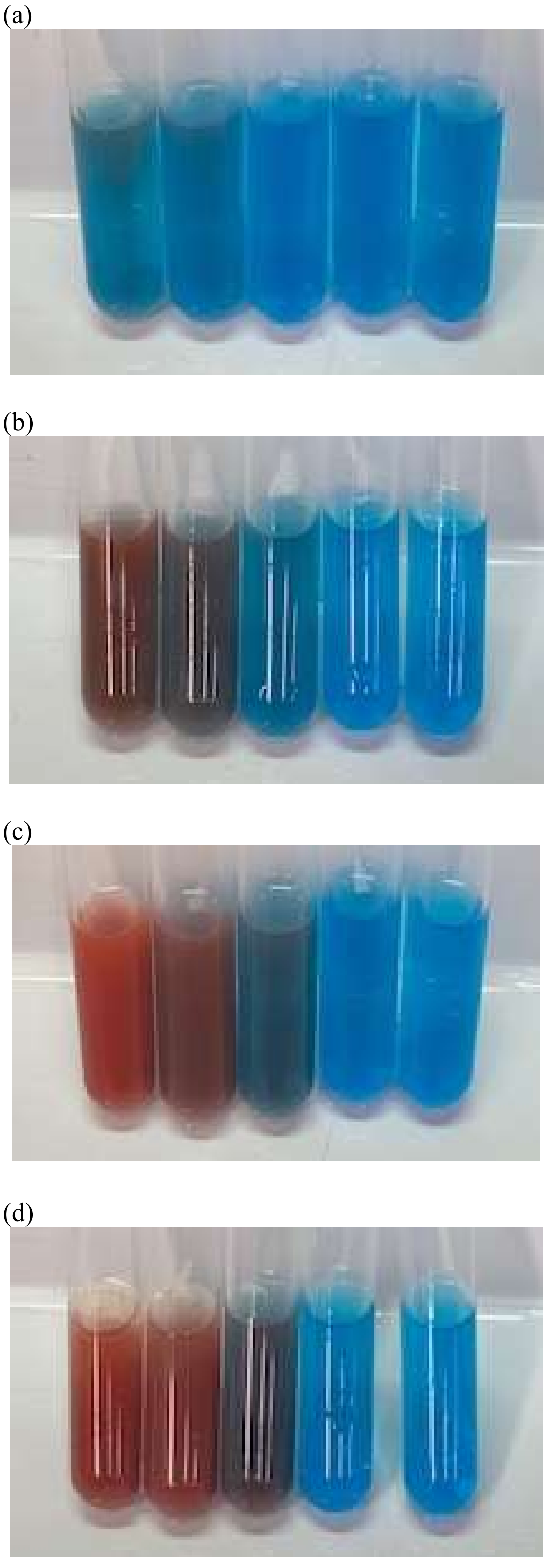

Fig. 6 Color changes in Benedict's reactions from left to right: fructose, WS, glucose, sucrose, and blank (a: after 1 min, b: after 2 min, c: after 3 min, d: after 5 min).

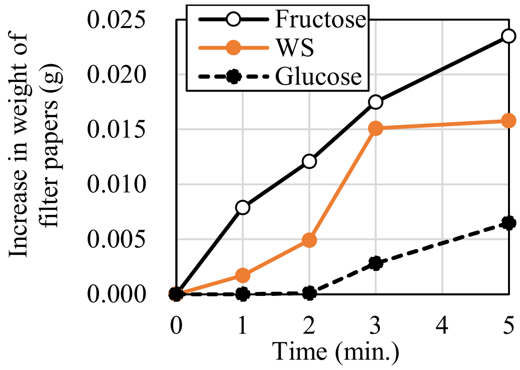

Fig. 7 Increase in the weight of filter papers after Benedict's reactions.

4.3 Electrochemical Evaluation

CV measurements were performed to examine the relation between reduction ability of sugars and their electrochemical oxidation behavior. The cyclic voltammogram for glucose-added system is shown in Fig. 8. The voltammogram shows that an oxidation current originating from the electrochemical oxidation of glucose appears at high potentials, and a significant oxidation current density of ~3 mA cm^{-2} is observed at 0.6 V. The measurement of the oxidation current of glucose using a CuO electrode has been reported in other studies [25], and similar results were obtained in this experiment, wherein its function as a catalyst for glucose oxidation was confirmed.

The cyclic voltammograms of the CuO-containing electrode in each sugar solution (potential range: -0.1 to 0.6 V (vs. Ag/AgCl)) are shown in Fig. 9. Significant oxidation currents were observed at 0.6 V for all sugars. Sucrose, similar to the other sugars, also showed oxidation currents. The details of the reaction mechanism of the electrochemical oxidation are still unclear. Although there was no significant difference in the current density, the voltammograms showed that the oxidation onset potentials differed among the different sugars.

In order to compare the oxidation onset potentials of voltammograms more clearly, potential range of the CV measurements was changed. The cyclic voltammograms of the CuO-containing electrode in each sugar solution (potential range: -0.1 to 0.2 V (vs. Ag/AgCl)) are shown in Fig. 10. The oxidation onset potential of each sugar was in the order of fructose < WS < glucose < sucrose. We presume that the higher the reducing property of the sugar, the lower the oxidation onset potential in the voltammograms. This order was particularly corresponding to that of the Benedict's reaction described in Fig. 7.

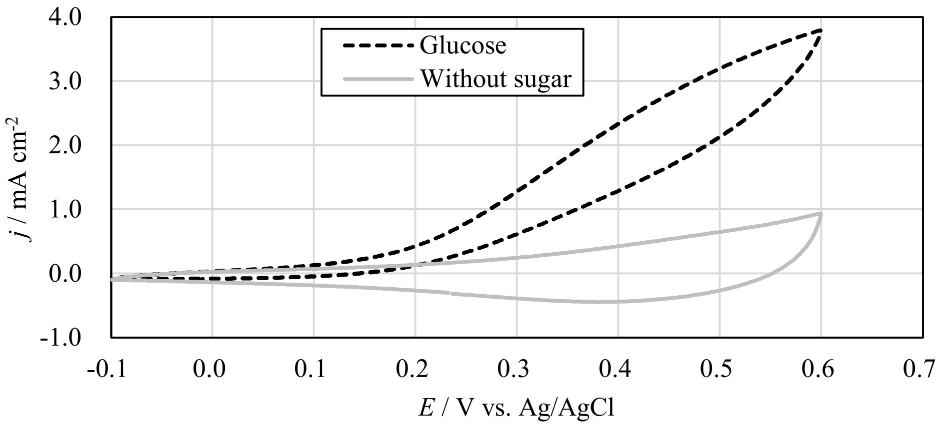

Fig. 8 Cyclic voltammograms of the CuO-containing electrode in the glucose solution (electrolite: 0.1 M NaOH, 10 mM glucose).

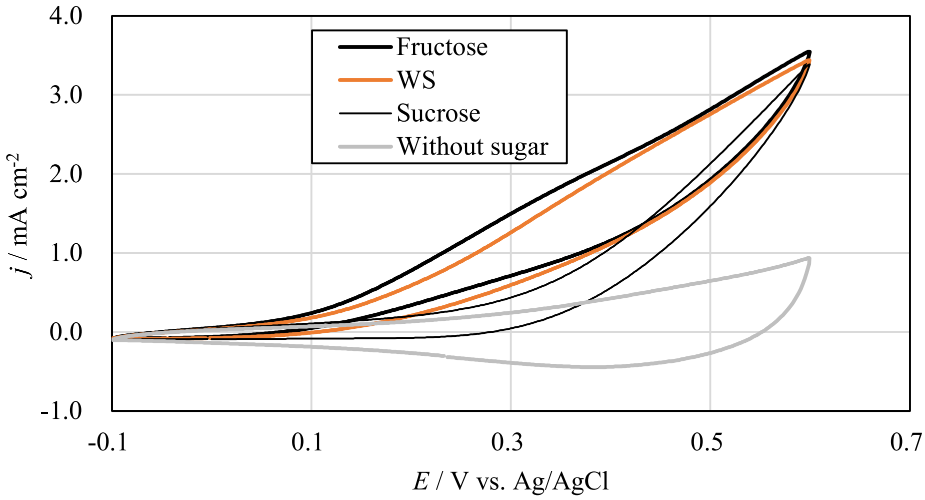

Fig. 9 Cyclic voltammograms of the CuO-containing electrode in each sugar solution (potential range: -0.1 to 0.6 V (vs. Ag/AgCl)).

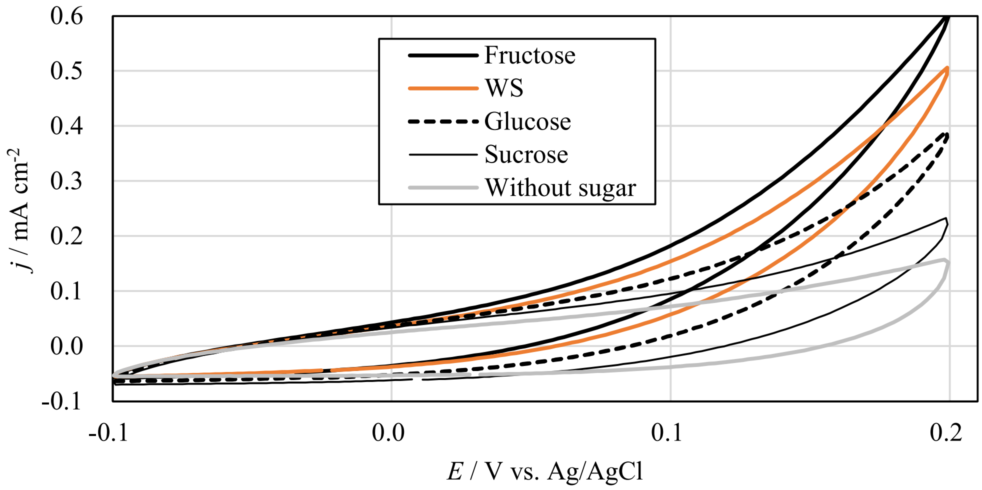

Fig. 10 Cyclic voltammograms of the CuO-containing electrode in each sugar solution (potential range: -0.1 to 0.2 V (vs. Ag/AgCl)).

5. CONCLUSIONS

Reduction ability of sugars (glucose, fructose, sucrose, and WS) under alkaline conditions were evaluated by the Fehling's reaction, Benedict's reaction, and electrochemical measurements. In the Fehling's reaction and Benedict's reaction, fructose resulted in higher reaction rates of Cu^{2+} reduction than those of glucose. High reductive abillity was also comformed in the case of WS. In electrochemical evaluations by cyclic volutammetry using CuO catalysts, the oxidation onset potential of each reducing sugar was in the order of fructose < WS < glucose. This result indicates that the higher the reducing property of the sugar, the lower the oxidation onset potential in the voltammograms. Thus, it can be expected that the electrochemical viewpoint can also help in the selection of the best sugar to add reinforced concrete.

In future anti-corrosion experiments using concrete specimens, we will investigate the strength of the concrete specimens in addition to the cohesion suppression caused by adding sugars to cement at the mixing stage.

6. ACKNOWLEDGMENTS

This research was supported by the Regional Innovation Ecosystem Program of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

The authors would like to thank Editage (https://www.editage.jp/) for the English language review.

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