

Investigations of Quantitative Reducibility Determination and Reducibility Variations of Neutral Hydrogen-Dissolved Water by Electrochemical Analysis

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Electrolysis using tap water(TW) in a batch type electrolyzer not separated into the anode chamber and cathode chamber produce neutral hydrogen-dissolved water(HDW) that dissolved gas hydrogen. Hydrogen in HDW was decreased with increased waiting time; subsequently, the decrement of hydrogen was measured by a dissolved hydrogen meter, open-circuit potential(OCP) measurement and square wave voltammetry(SWV). Neutral HDW had 219 ppb of hydrogen gas immediately after preparation; subsequently, the disappearance of dissolved hydrogen after 28 hours was verified by OCP measurements. Low concentration dissolved hydrogen, not detected by a dissolved hydrogen meter, was measured only by OCP. Oxidation-reduction properties in HDW were investigated by cyclic voltammetry(CV); consequently, HDW became a solution without further reducibility and similar to tap water after 30 hours. Oxidation peak of hydroxide ions, shown on cyclic voltammogram, measured in the potential range of -1.1 V~1.0 V, represent hydroxide ions produced during the CV measurement. The amount of reducibility of HDW by dissolved hydrogen was calculated with a galvanostatic oxidation method and it was determined as a quantitative reducibility.

Keywords: Hydrogen-dissolved water, Hydrogen-rich water, Neutral hydrogen-dissolved water, Reducibility, Reducibility measurement

1. INTRODUCTION

There is increased interest in the reducibility of hydrogen-dissolved water(HDW) that contains hydrogen gas. Previous studies have reviewed its beneficial relation as an antioxidant, pain reduction, and periodontitis[1-7]. A hydrogen gas-dissolved aqueous solution is called hydrogen-dissolved water(HDW)[8-10], also known as hydrogen-rich water[5-7], and hydrogen water[11-13]. There are

two methods to dissolve hydrogen into water: The first method blows hydrogen gas directly into the water from an external high-pressure tank (or a container) and is the most popular manufacturing method for HDW[9, 10]. The second method is an electrochemical manufacturing method for HDW that uses hydrogen gas produced by breaking down the chemical bond of water elements(hydrogen and oxygen) using electrical energy[5, 14]. An electrochemical manufacturing method for HDW is widely used for commercial devices due to simplicity, safety, and ease of use from not using high pressure container. There are two types of HDW produced by electrochemical methods according to chemical properties. One is called neutral electrolyzed HDW(or neutral HDW) prepared in an electrolyzer not separated into the anode chamber and cathode chamber. The other HDW is an alkaline hydrogen-dissolved water(electrolyzed reduced water) prepared in the cathode chamber of the electrolyzer separated into the anode chamber and the cathode chamber[14, 15]. Electrolyzed reduced water in alkaline drinks has a beneficial effect on gastritis as neutralizing agents by means of the chemically alkaline properties; however, has a limited range of use. Neutral HDW is widely used for therapeutic purposes or drinks [16, 17]. Previous research results show that HDW with a reductive gas has potential use in drinks, treatment solutions, and as a health supplement due to its antioxidant effects[18-22]. Researches on alkaline HDW and neutral HDW have been studied with a focus on reducibility. Studies on HDW have focused on treatment or clinical effects using the reducibility of HDW for medical use. Most studies report on the antioxidant and reducibility effects; however, there is inadequate detailed information on reducibility of hydrogen-dissolved solutions. To date, there are no studies have examined reducibility of HDW required for wide industrial use. And researche on the reducibility persistency has not reported yet also. Researchers need precise information that can describe reducibility to elucidate the safety of HDW and further feasible development. Electrochemical analysis is the most appropriate method for scrutiny of the reducibility of HDW that can directly produce an oxidation-reduction reaction of HDW and investigate changes. There is a study using an electrochemical method for reducibility of alkaline HDW(electrolyzed reduced water); however, a study on neutral HDW has not been reported yet [23].

This study performed scrutiny for the changes of decreasing reducibility as a function of waiting time and for the cause of reducibility occurring in neutral HDW prepared by electrolysis. The electrochemical measurements of HDW used square wave voltammetry(SWV), open circuit potential(OCP), cyclic voltammetry(CV), and galvanostatic oxidation. The redox properties can be explained by electrochemical measurements for the oxidation-reduction reaction of HDW. Variations in physicochemical properties of HDW were investigated by measuring changes in dissolved hydrogen concentration, pH, and oxidation reduction potential(ORP). The cause of reducibility in HDW was explained and the quantitative reducibility for dissolved hydrogen concentration was calculated through analysis and measurement. An electrochemical measurement will be applied to scrutinize of the reducibility of HDW; the results on reducibility will be useful data to explain the effects of HDW in various areas.

2. EXPERIMENTAL

Hydrogen-dissolved water(HDW) was prepared in a batch type of electrolysis apparatus using TW that is safe for the drinking and easily accessible. TW was left standing for 24 hours in the room condition and purified by activated carbon filter. To produce neutral HDW, the electrolysis was performed for three minutes at a constant current at room temperature without any electrolytes that increased conductivity of electrolytic solution in an electrolyzer that not separated into the anode chamber and cathode chamber. A dissolved hydrogen meter(ENH-1000, TRUSTLEX) recorded the concentration of dissolved hydrogen and the concentration changes as a function of waiting time. Square wave voltammetry(SWV) and open circuit potential(OCP) measurement helped identify the hydrogen concentration by an electrochemical method.

The changes of pH and oxidation reduction potential(ORP) were measured to investigate the pH and redox property of prepared neutral HDW. Reducibility changes depending on the changes of hydrogen concentration of the neutral HDW prepared by TW were explained by the changes of pH and ORP as a function of waiting time.

Cyclic voltammetry(CV) was performed to investigate reducibility changes in HDW and the redox property of TW was compared to neutral HDW. CV was measured in the half-cell with a three electrode by Radiometer (PGZ 301, VoltaLab) in open cell condition. All electrochemical measurements conducted in this study used high purity Pt foil as a working electrode(1 cm x 1 cm) and counter electrode(2 cm x 2 cm) and used an Ag/AgCl(3 M KCl) electrode as a reference electrode. The potential scan progressed at the rate of 20 mVs⁻¹. In order to determine the quantitative amount of reducibility of HDW, galvanostatic oxidation was performed at 25 μ A current density; then the changed reducibility of HDW were evaluated depending on the dissolved hydrogen as a function of waiting time. The reduction charge amount was calculated by the reducibility from the oxidation current density and time of completed oxidation of the HDW.

3. RESULTS AND DISCUSSION

Neutral hydrogen-dissolved water(HDW) was prepared by electrolyzing tap water(TW) in an electrolyzer was not separated into the anodic chamber and cathodic chamber by a diaphragm. Changes of hydrogen concentration in HDW produced by the electrochemical method were investigated using a hydrogen detector over waiting time. Figure 1 indicates the changes in hydrogen concentration. The hydrogen concentration of HDW after as-preparation was 219 ppb; however, it continually decreased over 12 hours until dissolved hydrogen was not detected. Hydrogen in HDW showed a tendency to decrease at a constant speed in an open cell. The slope of decreasing dissolved-hydrogen concentration indicates the decreased rate of hydrogen concentration at 18.59 ppb/h. The concentration of hydrogen in the TW never appeared; consequently, hydrogen dissolved in HDW is explained as hydrogen produced from water molecules decomposed by an electrolysis mechanism. Hydrogen dissolved in HDW disappears over time; therefore, it turns out that the effects of HDW exist for a limited time after production.

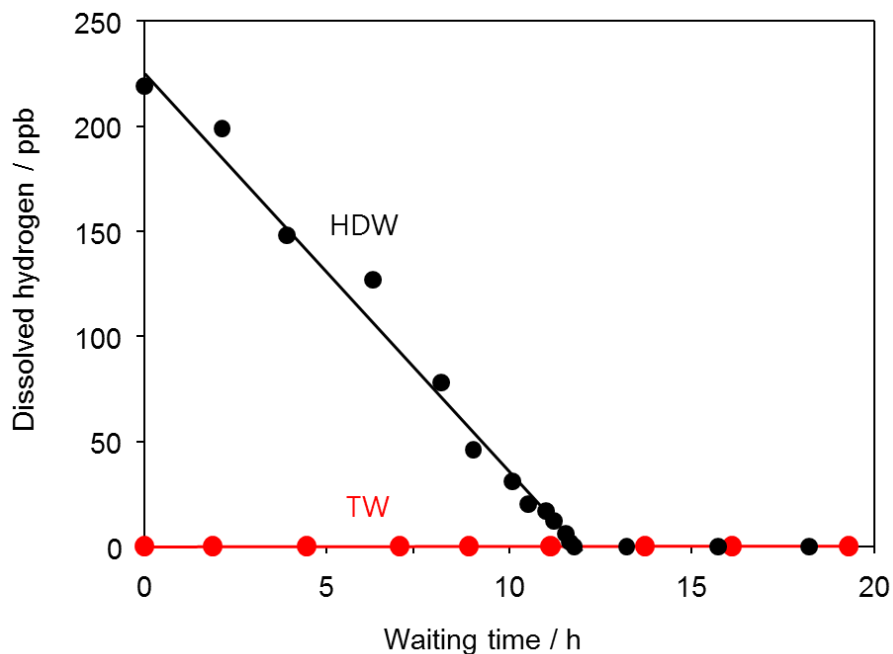


Figure 1. The variations of hydrogen dissolved concentration of tap water(TW) and hydrogen-dissolved water(HDW) prepared by electrolysis as a function of waiting time.

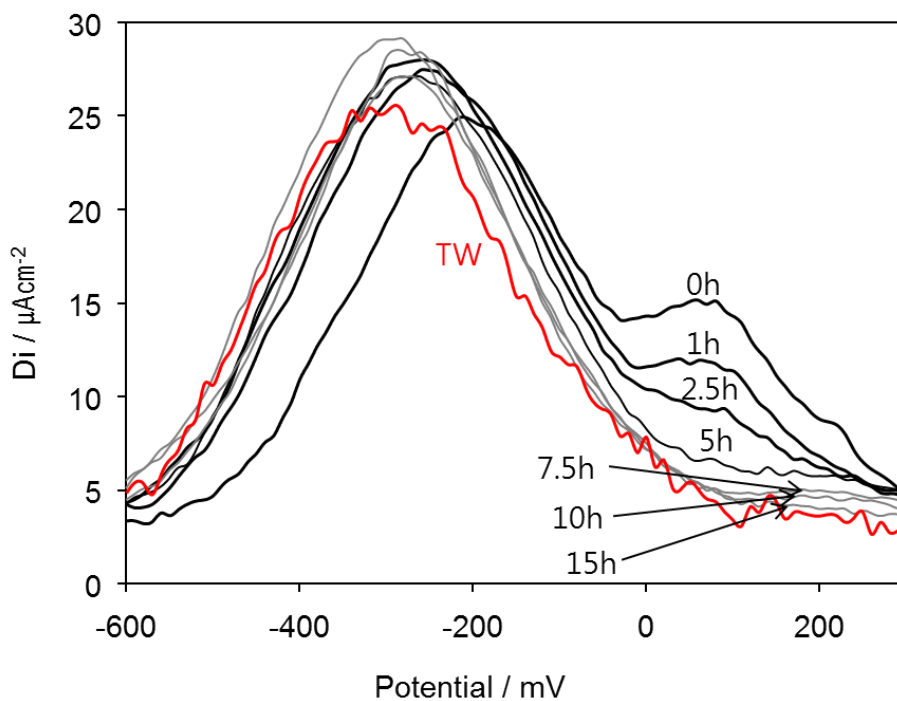


Figure 2. Square wave voltammograms(SWV) of hydrogen-dissolved water(HDW) of various waiting times and tap water(TW).

Square wave voltammetry(SWV) was performed to detect the hydrogen dissolved in HDW by an electrochemical method and investigate concentration changes over waiting time. Figure 2 indicates the square wave voltammograms measured over time after producing HDW. The oxidation peak of hydrogen dissolved in HDW appeared around 100 mV potential range and gradually decreased over

waiting time. An oxidation peak of dissolved hydrogen did not appear in HDW waiting over 5 hours. This coincides with former studies on the detection of hydrogen dissolved in electrolyzed reduced water using SWV[23]. Electrochemical SWV is superior to cyclic voltammetry(CV) as a hydrogen detection method; however, this electrodynamic measurement that has weakness on detection of traces of hydrogen low concentration. Figure 1 and figure 2 indicates that electrodynamic SWV can detect a higher concentration of hydrogen.

An open circuit potential (OCP) was measured as an electrostatic measurement to supplement the detection limit of dissolved hydrogen using SWV as an electrodynamic measurement. Figure 3 indicates the changes in the OCP of TW and HDW measured for 110 hours. The changes of OCP occur according to properties of chemical species absorbed to electrodes contained in an electrolyte solution that can explain concentration changes in hydrogen gas. The OCP of as-prepared HDW indicates that it was prepared -276 mV reductive solution and that gradually increased. After about 28 hour increasing OCP of HDW, it does not show significant changes and it maintains a constant OCP of near 100 mV. The increased OCP indicates the time of gradually decreasing hydrogen dissolved in HDW; in addition, the stable OCP indicates the disappearance of all dissolved hydrogen. The OCP of TW did not show significant changes and it maintained a constant OCP over waiting time for 110 hrs. The change in the OCP of HDW and TW shows that HDW lost its hydrogen and reducibility and become a solution similar to tap water. The measurement of the OCP of HDW explains the longer hydrogen-dissolved period than the results measured by the dissolved hydrogen meter or SWV. The results indicate that the electrostatic OCP is a useful measurement method for a low-concentration hydrogen solution.

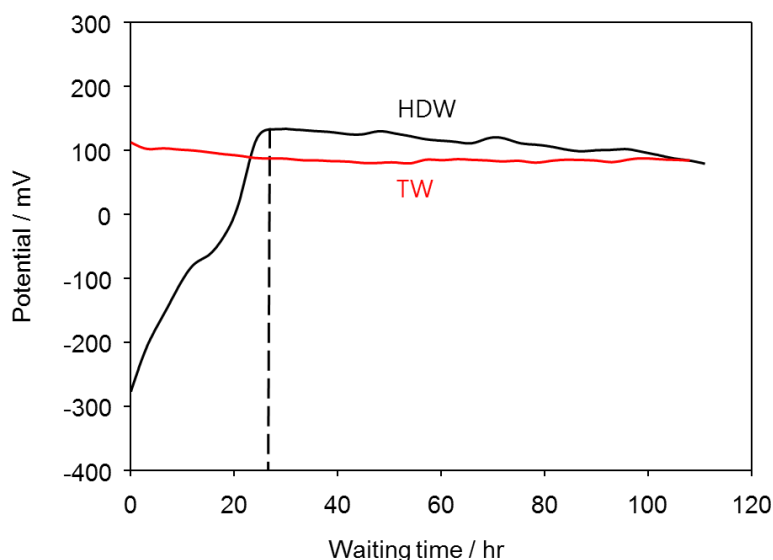


Figure 3. Open circuit potential(OCP) curves of hydrogen-dissolved water(HDW) and tap water(TW) as a function of waiting time.

The oxidation reduction potential(ORP) and pH of HDW produced by the electrochemical method were measured at various waiting time (see Figure 4). The pH of HDW did not indicate significant changes for 120 hours and it maintained a value of 7.5 ± 0.2 . These results indicate that

HDW was produced with a neutral solution that had the same pH level of TW used as a raw material and a stable solution without pH change over waiting time. It is expected to be used in various areas than electrolyzed reduced water that is alkaline HDW because neutral HDW has no pH limit[23].

The oxidation reduction potential(ORP) of electrolyzed HDW prepared by electrolysis was measured a -229 mV of the reductive solution; however, for 40 hours, the ORP increased gradually(Figure 4). The ORP increased to about 100 mV and was constant for 120 hours. The measurement results from the ORP indicated that the HDW prepared by electrolysis was a high reducibility solution; however, it gradually lost its reducibility over time and became a solution similar to tap water. The use of HDW as a reductive solution or solvent shows that the significant effect of reducibility by high-concentration dissolved hydrogen can be expected only when it is used quickly after production. There is the possibility of a complicated effect of reducibility and alkalinity in the case of using electrolyzed reduced water as a solution or a solvent; neutral HDW is expected to have more advantages when using a solution or a solvent and expecting only a reducibility effect.

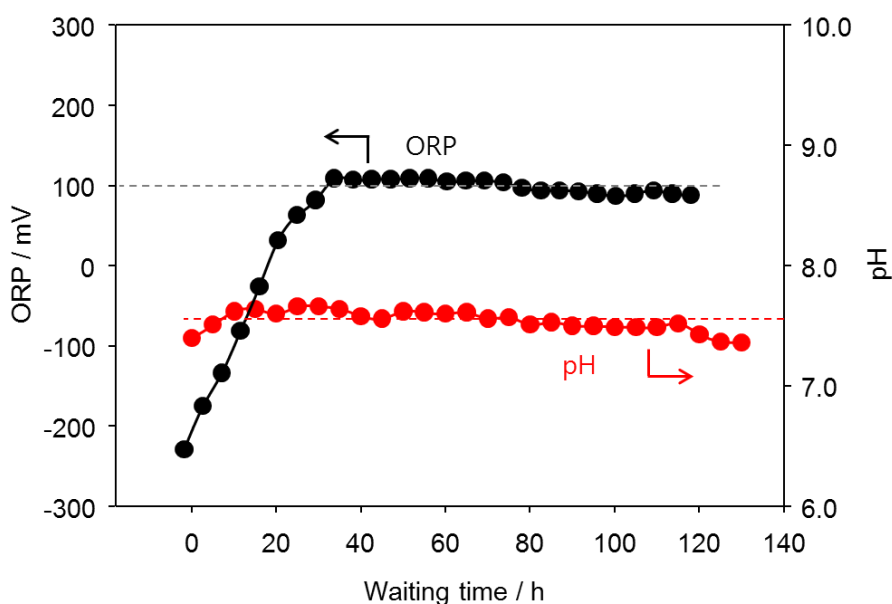


Figure 4. Variation curves of pH(red) and ORP(black) in hydrogen-dissolved water(HDW) as a function of waiting time.

The redox properties of HDW changed for waiting time were investigated with electrochemical cyclic voltammetry(CV) and the obtained cyclic voltammograms were compared to tap water (see Figure 5 (a) and (b)). A typical cyclic voltammograms of aqueous solution had been measured and the similar changes to cyclic voltammograms of electrolyzed reduced water over waiting time had been obtained[23]. Cyclic voltammograms of as-prepared HDW measured in the potential range of -1.1 V ~ 0.0 V have shown a higher redox current density value than tap water. Redox current density gradually was decreased over waiting time and became a similar redox current density of TW after 20 hours. As the concentration of dissolved hydrogen gas increased, the current density of the reversible process of

decomposition into hydrogen gas of water molecules in HDW was increased. When the concentration of dissolved hydrogen gas in HDW decreased, the current density of the reversible process was decreased too. A reduction of the oxide layer of a platinum electrode occurs below -0.1 V of potential range if CV is conducted into the reduction direction. Because the effect of a high-concentration reductive hydrogen gas dissolved in HDW, the reduction of an oxide layer of platinum electrode was finished at -0.54 V. In the TW, the reduction of an oxide layer of platinum electrode was extended up to -0.70 V because the reduction progressed only as an electrochemical reaction of voltammetry. The reduction of the oxide layer of platinum gradually extended and shows a similar result to the TW after 30 hours waiting time. The reducibility of HDW was decreased as dissolved hydrogen gas was disappeared.

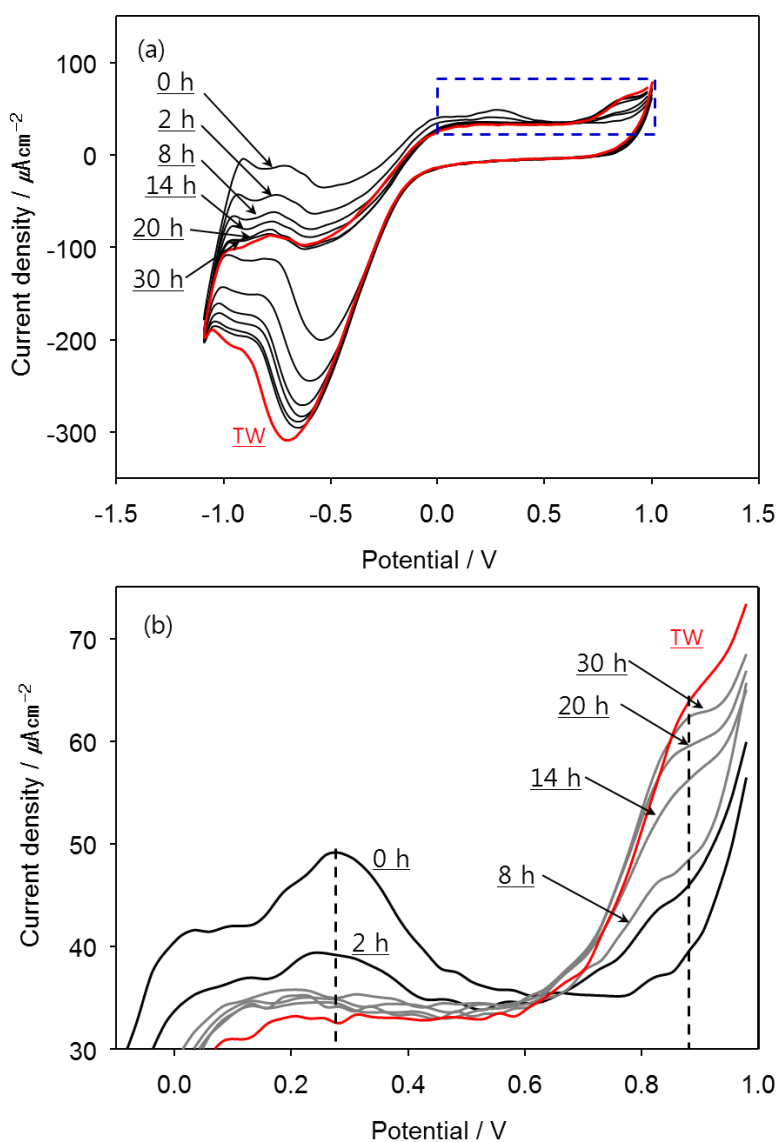


Figure 5. Cyclic voltammograms of TW(red) and HDW(black) obtained at various waiting times.

Figure 5 (b) shows the magnified cyclic voltammograms of the oxidation process of HDW, measured in the potential range of 0.0 V~1.0 V. The oxidation peak on the 0.27 V potential was an oxidation peak of dissolved hydrogen gas. The HDW waiting for over 2 hours did not show an

oxidation peak of hydrogen gas because CV was not easy to detect low hydrogen concentration. Whereas, the oxidation peak of hydroxide ions, usually does not appeared from the neutral HDW after as-preparation, appeared on the 0.85 V potential and increased gradually over waiting time. HDW has a higher hydrogen concentration after as-preparation; hydroxide ions produced during cyclic voltammetry (CV) in the potential range of -1.1 V ~ 0.0 V by the water decomposition process react with hydrogen gas and became water; consequently, oxidation peak of hydroxide ion was not observed. However, the oxidation peak of hydroxide ions was appeared after 2 hours and the intensity of peak was increased over time. With the hydrogen concentration decreasing, the hydroxide ion was not neutralized in the process of cyclic voltammetry measurement and the oxidation peak was increased gradually. HDW waiting for over 30 hours showed an oxidation peak of hydroxide ions similar to TW because most hydrogen gases dissolved in HDW were removed.

In order to investigate cyclic voltammograms that have not affected on hydroxide ions produced during cyclic voltammetry (CV) measurement in the potential range of -1.1 V ~ 1.0 V, the measurement of cyclic voltammetry (CV) was conducted in the potential range of -0.1 V ~ 1.0 V and resulted cyclic voltammograms were represented in figure 6. Cyclic voltammograms of TW and other HDWs show no oxidation and reduction peak except oxygen generation at 0.9 V and the flat curve shows an electric double layer of electrode surface. The reason for higher cyclic voltammograms in the oxidation direction of HDW for 0 hour and 1 hour waiting is similar to that the higher hydrogen concentration of HDW shows a higher current density of water decomposition reaction. An electric double layer similar to cyclic voltammograms of TW was observed in HDWs waiting over 3 hours with hydrogen concentration decreasing. In the process of preparation of neutral HDW, hydroxide ions and hydrogen ions produced in the cathode and anode during electrolyzing process are neutralized immediately and they were not detected electrochemically. These result shown in figure 5(b) could be explain the oxidation peak of hydroxide ions corresponding to the hydroxide ions was produced during cyclic voltammetry measurements.

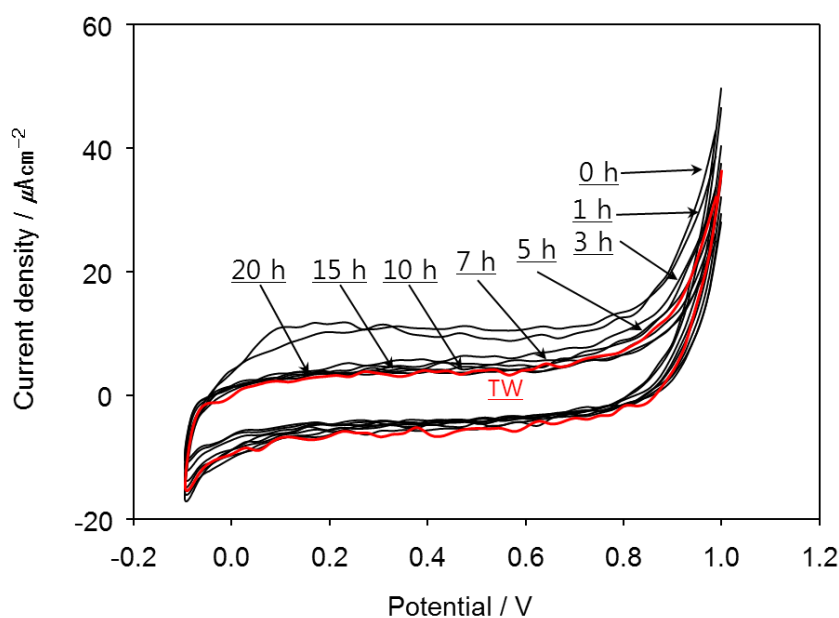


Figure 6. Cyclic voltammograms of the TW(red) and HDW(black) obtained at various waiting times.

OCP or ORP is adequate to explain the strength of reducible energy for reducibility of HDW; however, a quantitative measurement method is required to explain the amount of reducibility. In order to measure the quantitative amount for reducibility of HDW, the electrochemical galvanostatic oxidation was conducted to determine the reducibility of HDW [23].

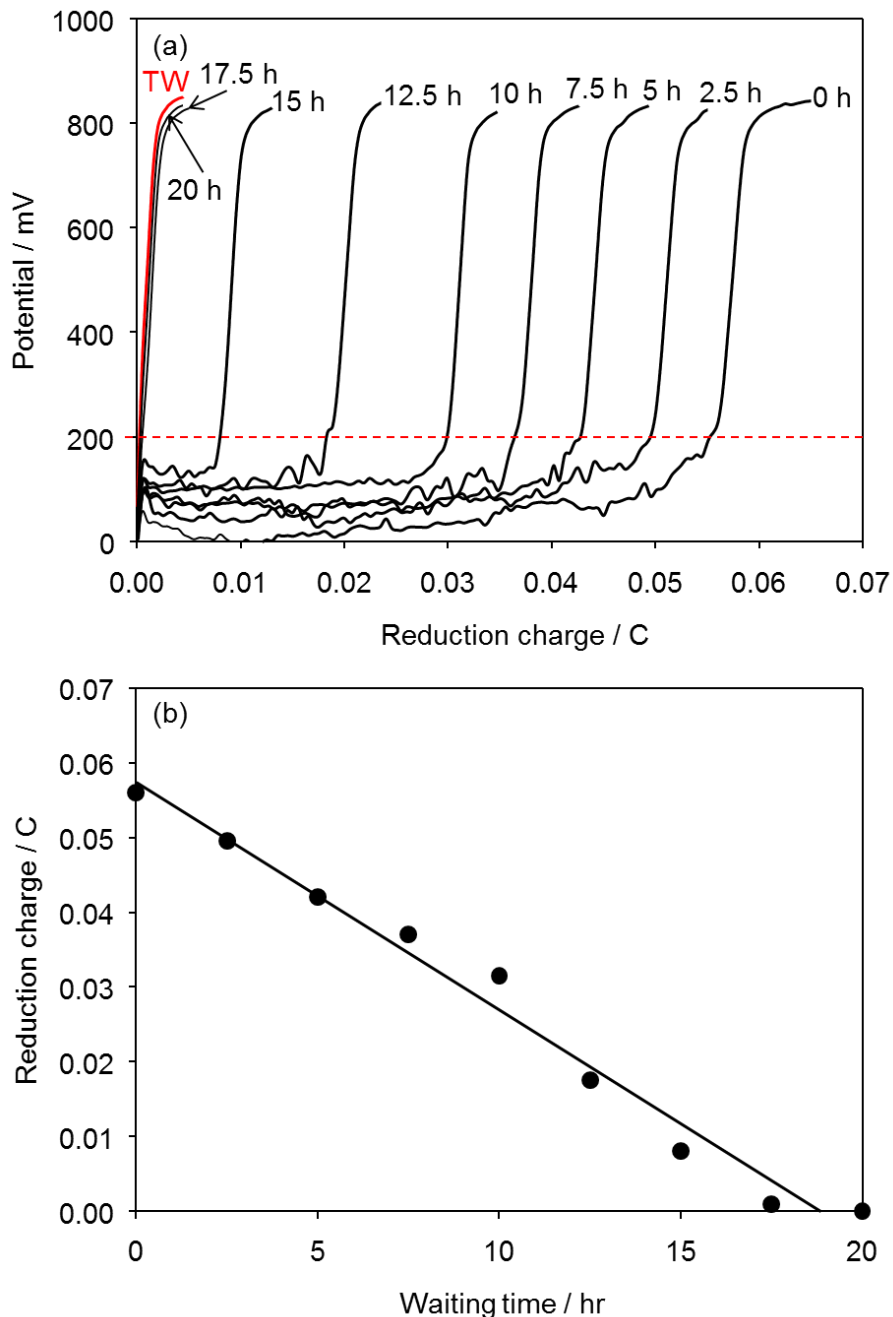


Figure 7. Galvanostatic oxidation curves of tap water(TW) and hydrogen-dissolved water(HDW) at various waiting times.

Figure 7 (a) shows galvanostatic oxidation curves of the tap water and of the HDWs measured at various waiting time. After starting galvanostatic oxidation, oxidation curve of the TW was increased up to over 800 mV immediately and did not show other oxidation reaction. The potential

range of electrochemical oxidation of reductive hydrogen was verified below 800 mV from the results of CV in Figure 5 (b); therefore, the terminal point of measuring of galvanostatic oxidation curve was set 800 mV. When the potential increasing to 200 mV after the oxidation of reductive chemical species involved in HDW, the galvanostatic oxidation curve rapidly rose; therefore, the potential determining the amount of reducibility of HDW was 200 mV. The amount of reducibility of HDW was calculated at 0.056 C immediately after as-preparation. Figure 7 (a) shows that the galvanostatic oxidation curve of HDW shortened gradually with waiting time increasing. The reducibility of HDW was decreased with the waiting time increasing gradually then, it almost disappeared after 17.5 hours. The results show that the decrease of hydrogen dissolved in HDW is why the reducibility of HDW disappeared. And it coincides with results of former dissolved-hydrogen concentration, OCP, and ORP measurements. Figure 7 (b) shows that reducibility amount of each HDWs obtained by calculating the end point of the oxidation according to the various waiting time by galvanostatic oxidizing. The reducibility decrease of HDW also linearly reduced proportional to the increase in waiting time and was similar to the dissolved hydrogen-concentration changes.

4. CONCLUSION

We had investigated the reducibility of neutral hydrogen-dissolved water(HDW) prepared in a batch type electrolyzer that was not separated into the anodic chamber and the cathodic chamber. The changed reducibility was investigated according to the decrease of dissolved hydrogen with waiting time. The change of reducibility in HDW is explained by the dissolved-hydrogen concentration, the oxidation reduction potential(ORP) measurement and various electrochemical investigations.

More than 200 ppb of high-concentration hydrogen dissolved in as-prepared HDW was detected after as-preparation by dissolved hydrogen meter and electrodynamic square wave voltammetry(SWV); however, decreased low-concentration hydrogen was detected only by electrostatic open circuit potential(OCP) measurement. From the cyclic voltammetry(CV) measured in the potential range of -1.1 V~1.0 V , it was explained that the high-concentration hydrogen gas dissolved in HDW inhibit the oxidation of platinum electrodes. Because the dissolved hydrogen gas in HDW reduces the oxide layer of electrode the oxidation peak of hydroxide ion produced during measurement of cyclic voltammetry did not detected. Hydroxide ions were not detected in cyclic voltammograms measured in the potential range of -0.1 V~1.0 V, it explain that hydroxide ions and hydrogen ions produced during electrolysis has been neutralized and neutral HDW was generated. The amount of reducibility caused by hydrogen dissolved in HDW was calculated by galvanostatic oxidation and was investigated as a function of waiting time. The decreasing hydrogen concentration is proportional to the calculated reducibility of quantitative amount of HDW.

References

1. Y. Sato, S. Kajiyama, A. Amano, Y. Kondo, T. Sasaki, S. Handa, R. Takahashi, M. Fukui, G. Hasegawa, N. Nakamura, H. Fujinawa, T. Mori, M. Ohta, H. Obayashi, N. Maruyama and A. Ishigami, *Biochem. Biophys. Res. Commu.*, 3 (2008) 346.

2. A. Kitamura, S. Kobayashi, T. Matsushita, H. Fujinawa and K. Murase, *British J. Radiology*, 83 (2010) 509.
3. A. Ghanizadehand M. Berk, *Med. Gas Res.*, 3 (2013) 11.
4. T. Matsushita, Y. Kusakabe, A. Kitamura, S. Okada, K. Murase, *Jpn. J. Radiol*, 29 (2011) 503.
5. K. Kasuyama, T. Tomofuji, D. Ekuni, N. Tamaki, T. Azuma, K. Irie, Y. Endo, M. Morita, *J. Clin. Periodontol.*, 38 (2011) 1085.
6. A. Nakao, Y. Toyoda, P. Sharma, M. Evans and N. Guthrie, *J. Clin. Biochem. Nutr.*, 46 (2010) 140.
7. A. Shimouchi, K. Nose, M. Shirai and T. Kondo, *Adv. Expert. Med. Biology*, 737 (2012) 245.
8. R. Asada, K. Kageyama, H. Tanaka, H. Matsui, M. Kimura, Y. Saitoh and N. Miwa, *Oncology Reports*, 24 (2010) 1463.
9. Y. Saitoh, Y. Yoshimura, K. Nakano and N. Miwa, *Experimental Oncology*, 31 (2009) 156.
10. S.-I. Yamaura, T. Yamamoto, H. Kimura and A. Inoue, *Mat. Trans.*, 46 (2005) 1687.
11. V. B. Ptashnik, T. Yu. Dunaeva and V. A. Lukoshkin, *Kinetica and Catalysis*, 27 (1986) 426.
12. I. Ohsawa, K. Nishimaki, K. Yamagata, M. Ishikawa and S. Ohta, *Biochem. Biophysic. Res. Commu.*, 377 (2008) 1195.
13. Y. Gu, C.-S. Huang, T. Inoue, T. Yamashita, T. Ishida, K.-M. Kang and Nakao, A., *J. Clin. Biochem. Nutrition*, 46 (2010) 269.
14. S. Shirahata, T. Hamasaki and K. Teruya, *Trends in Food Science & Technol.*, 23 (2012) 124.
15. J. Xue, G. Shang, Y. Tanaka, Y. Saihara, L. Hou, N. Velasquez, W. Liu¹, and Y. Lu, *BMC Complement. Alternat. Med.*, 14 (2014) 81.
16. L. Qian[□], J. Shen[□], Y. Chuai and J. Cai, *Int. J. Biolog. Sci.*, 9 (2013) 887.
17. M. P. Schoenfeld, R. R. Ansari, J. F. Zakrajsek, T. R. Billia, Y. Toyoda, D. A. Wink and A. Nakao, *Med. Hypotheses*, 76 (2011) 117.
18. J.-Y. Zhang, Q.-F. Wu, Y. Wan, S.-D. Song, J. Xu, X.-S. Xu, H.-L. Chang, M.-H. Tai, Y.-F. Dong, C. Liu, *World J. gastroenterology*, 20 (2014) 1614.
19. S. Kajiyama, G. Hasegawa, M. Asano, H. Hosoda, M. Fukui, N. Nakamura, J. Kitawaki, S. Imai, K. Nakano, M. Ohta, T. Adachi, H. Obayashi, T. Yoshikawa, *Nutrition Res.*, 28 (2008) 137.
20. K. Noda, Y. Tanaka, N. Shigemura, T. Kawamura, Y. Wang, K. Masutani, X. Sun, Y. Toyoda, C. A. Bermudez and A. Nakao, *European Soc. Organ Transplantation*, 25 (2012) 1213.
21. L. Qian, F. Cao, J. Cui, Y. Wang, Y. Huang, Y. Chuai, L. Zaho, H. Jiang and J. Cai, *J. Radiat. Res.*, 51 (2010) 741.
22. Q. Sun, T. Kawamura, K. Masutani, X. Peng, Q. Sun, D. B. Stolz, J. P. Pribis, T. R. Billiar, X. Sun, C. A. Bermudez¹, Y. Toyoda, and A. Nakao, *Cardiovascular Research*, 94 (2012) 144.
23. W.-K. Choi. *Int. J. Electrochem. Sci.*, 9 (2014) 6648.