

Electrochemical Characterizations of the Reducibility and Persistency of Electrolyzed Reduced Water Produced from Purified Tap Water

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We use tap water(TW) electrolysis to produce an alkaline and reducible aqueous solution known as electrolyzed reduced water (ERW). To explain the variations of physicochemical properties, we investigated the concentration change of hydrogen gases and hydroxide ions generated in cathodic electrolysis and dissolved in electrolyzed reduced water. Alkalinity and alkaline persistency against the waiting time of the prepared ERW were investigated as a pH measurement and electrochemical analysis after standing for 140 hrs. The higher reducibility of as-prepared ERW was evaluated by oxidation reduction potential (ORP) values and analyzed by cyclic voltammetry electrochemically; the available reducibility period of ERW was investigated using ORP measurements and electrochemical analysis after being left for 140 hrs. Changes in cyclic voltammograms and the square wave voltammograms were used for redox characterizations and the hydrogen detection of ERW as an electrochemical method. A quantitative measurement of reducibility for ERW was performed using galvanostatic oxidation and 0.027 C was obtained as an electrochemical reducible charge amount.

Keywords: Electrolyzed water, Electrolyzed reduced water, Functional water, Reducibility, Reducibility persistency

1. INTRODUCTION

Electrolyzed reduced water (ERW) or electrolyzed oxidized water (EOW) produced by water electrolysis is called electrolyzed water, electrolyzed ionic water, or functional water. Electrolyzed water is prepared as an alkaline, acidic or neutral solution according to engineering design and electrolysis device configuration [1-4]. Reduced water and oxidized water are prepared by electrochemical reduction and oxidation which occur irreversibly on the surface of the anode and cathode installed in an electrolytic cell. The hydrogen gas and oxygen gas generated on the cathode

and anode during water electrolysis are dissolved easily in electrolyzed oxidized water and electrolyzed reduced water [4-6]. Neutral electrolyzed water is prepared by the recombination of the anion and cation generated from the redox reaction of the anode and cathode in the unseparated electrolytic cells as cathode chamber and anode chamber. When water is electrolyzed in electrolytic cells divided into an anode chamber and a cathode chamber by a charge exchangeable diaphragm, the reduced water is produced in the cathode chamber and the oxidized water is produced in anode chamber. Alkaline hydroxide ion (OH^-) is generated by the reduction mechanism of water and dissolved in the electrolyzed reduced water of the cathode chamber; the acidic proton (H^+) is also generated by the oxidation mechanism and then dissolved in electrolyzed oxidized water in the anode chamber. Electrolyzed water contains some gases and ions with distinct physicochemical properties versus non-electrolyzed raw water. Acidic electrolyzed oxidized water is effective for disinfection [7, 8], sterilization, and cleaning; in addition, alkaline electrolyzed reduced water with an effective reducibility can be used for medical purposes, wafer washing, and drinking [8-10]. Further studies on the antioxidant effect using the reducibility of electrolyzed reduced water have been introduced by other researchers after the discovery by S. Shirahata [4, 11-13]. The effect and result of the dialysate on diabetes using electrolyzed reduced water were reported by K.-C. Huang and H. K. Kim [14, 15]. Research has indicated effective reducibility results using electrolyzed reduced water and examined potential applications. Most of ERW studies were focused on the applications of ERW and reported just the effect and result without the detail analysis and explanation about reducibility of ERW. For the effective utilization of ERW, a concentrated study to the reducibility is necessary but it has not reported for the detail explanation of redox property of ERW up to now. The electrochemical study and data for the ERW redox properties could assist an effective and safe use in various applications. Electrochemical measurement is a direct oxidation reduction method for the ion, gas and solvent included in solution. Consequently a lot of information of ERW reducibility obtained by electrochemical analysis will be usefully used for ERW researchers in various applications. To obtain the unresearched reducibility information and data of ERW by electrochemical analysis, this study was performed using as-prepared ERW for long waiting time.

In this study, the properties of ERW are discussed from the variation of the alkalinity and the persistency of reducibility according to ions and gases generated by water electrolysis. The available persistency of electrolyzed reduced water was estimated as the values of pH and oxidation reduction potential (ORP) which indicate concentration variations of dissolved ions and gases against increased waiting time [16-18]. Cyclic voltammetry and square wave voltammetry investigated reducibility changes of ERW and detected reducible hydrogen gas at low concentrations dissolved in ERW. The magnitude of reducibility for ERW was calculated using the galvanostatic oxidation of reducible chemicals dissolved in ERW. The quantitative value of reducibility obtained in electrochemical analysis represents an applicative purpose for various ERW application fields.

2. EXPERIMENTAL

Alkaline electrolyzed reduced water was prepared by an electrolysis apparatus that did not dissolve any electrolytes. To minimize impurities, tap water (TW) was purified by a composition filter

filled with activated carbon and was supplied to a commercial electrolyzed water generation system (HU50, OSG corporation Co., Ltd). Purified tap water was supplied continuously into the anode chamber and cathode chamber of a separated electrolytic cell by diaphragm. The electrolysis status of prepared ERW was determined as drinking, cleansing or rinsing by adjusting the apparatus.

To evaluate the persistency of the reducibility and alkalinity of prepared ERW, the variation of pH and ORP was measured for 140 hrs at room temperature. The pH and ORP variations against waiting time of the alkaline ERW with reducibility produced by neutral tap water describe the concentration change of the hydroxyl ion(OH⁻) and hydrogen gas(H₂) and explain the change of related redox property of them [19]. In the cathode chamber, the hydrogen gas(H₂) and hydroxyl ion(OH⁻) generated by cathode reaction are dissolved into electrolyzed reduced water.

The concentration of hydrogen gas dissolved in electrolyzed reduced water was measured by a hydrogen detector in order to explain the electrochemical redox property. The voltammograms obtained by cyclic voltammetry (CV) was used to compare the redox properties of tap water and ERW [20]. Cyclic voltammetry was measured at half-cell using three electrodes by a Radiometer (PGZ 301, VoltaLab) under opened air conditions with a 20 mV s⁻¹ scan rate. High purity platinum foils were used as an working electrode (1 cm x 1 cm) and counter electrode (2 cm x 2 cm). Potentials were measured against an Ag/AgCl(3M KCl) reference electrode. The magnitude of quantitative reducibility for ERW and tap water was measured and compared by the galvanostatic oxidation of 2.5 μA current density[21]. Low concentration hydrogen gas dissolved in ERW was analyzed by square wave voltammetry with 1 mV s⁻¹ scan rate, 2 mV amplitude and 50 mV pulse [22, 23]. Hydrogen dissolved in ERW was identified by comparing to a square wave voltammogram of the hydrogen injected water.

3. RESULTS

Electrolyzed reduced water (ERW) was prepared with a commercial electrolysis apparatus equipped an electrolyzer which was separated by a polymer separator as a cathode chamber and anode chamber. As a raw material the supplied tap-water was filtered by a carbon composition filter prior to electrolysis and the as-prepared ERW was an alkaline solution of pH 9.0. The pH variation of prepared ERW was measured in an opened cell under room temperature and a pH curve was obtained as a function of waiting time (see Fig. 1). Higher alkaline pH(9.0) of as-prepared ERW decreased to neutral pH (7.5) ERW after 40 hrs; consequently, a stable pH persisted without variation for 100 hrs. However, tap water pH maintained neutral values without variation in the measuring period. A linear pH decrement of alkaline ERW could explain the continuous decrease of hydroxyl ion(OH⁻) which produced a cathode electrolysis procedure during the waiting time. [16] The decrease of chemical species produced in the electrolysis procedure could be considered since chemical or physical properties have changed. The pH decrement related to change of chemical species generated in the electrolysis shows that the physicochemical property of as-prepared ERW was not maintained and was neutralized like tap water.

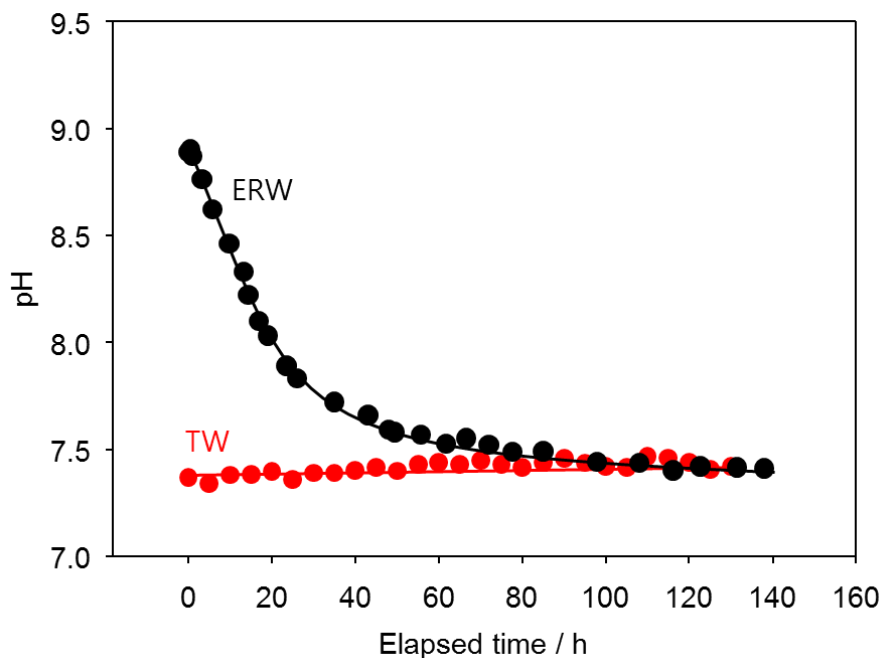


Figure 1. The pH variation profiles of tap water and prepared electrolyzed reduced water as a function of waiting time.

Chemical species, ion(H^+ , OH^-) and gas(H_2 , O_2), different from water molecules, are generated by electrolysis and dissolved in ERW, because the electrolysis of tap water by irreversible oxidation and reduction could change the chemical structure of water molecules. ERW containing ion or gas generated by splitting of water molecules represents a redox property different from tap water. The measured ORP value of ERW explains the reducibility of ERW because ORP could describe the tendency of a solution to lose or gain electrons. The hydrogen gas and hydroxide ion(OH^-) generated by electrolysis were dissolved in ERW and shows a different electrochemical ORP (redox potential) than tap water.

Figure 2 shows the change of ORP of prepared ERW and measured as a function of waiting time under an opened state. We measured the ORP -231 mV of the prepared ERW that indicated a higher reduction state than tap water. It markedly increased to neutral ORP (c.a. 130 mV) for about 40 hrs and persisted continuously without fluctuation. The decrement of reductive species contained in ERW was estimated from the increased ORP value for about 40 hrs which signified a decrement of reducibility. The hydrogen gas produced by the electrochemical reaction in the cathode chamber represents a reducible chemical species dissolved in ERW[24, 25]. The lower ORP value signifies a high reducibility of as-prepared ERW and increased linearly due to the decrease in dissolved hydrogen gas during the waiting time. About 40 hrs later, a stable ORP curve without fluctuation indicated a disappeared reducibility by diminished hydrogen gas dissolved in as-prepared ERW. Like the pH result, a similar result was investigated by ORP measurement because the physicochemical properties of the as-prepared ERW disappeared during the 40 hr procedure. However, high ORP value (400 mV) signifying an oxidative solution of tap water decreased for 40 hrs gradually and represented stable ORP value of neutral solution without fluctuation.

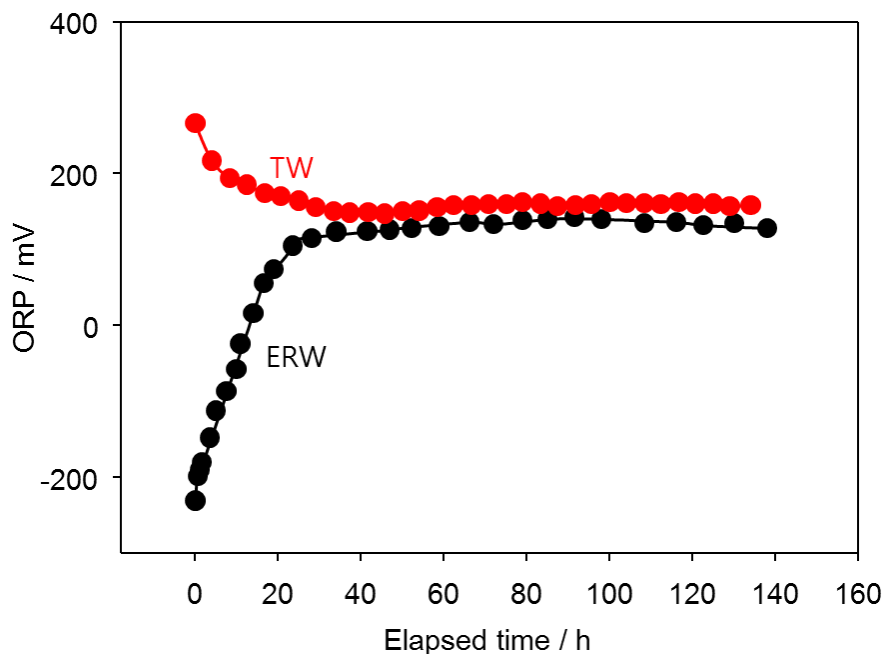


Figure 2. The ORP variation profiles of tap water and prepared electrolyzed reduced water as a function of waiting time.

The reducible hydrogen and concentration variations as a function of waiting time were investigated to find the causative substance representing a reducibility of ERW. The concentration of dissolved hydrogen generated by the cathodic mechanism during the ERW production was measured by a hydrogen detector and plotted (see Fig. 3). The 193 ppb hydrogen produced by cathode reaction was dissolved in as-prepared ERW and decreased linearly for about 12 hrs. The concentration change of reducible hydrogen gas could be associated with ORP variation. The decrement of hydrogen concentration increases ORP because ORP is a property of the aqueous solution that depends on concentration and does not depend on the chemical species [17, 18]. The concentration decrease of dissolved hydrogen could be a reason for the diminished reducibility of ERW. The detected time of dissolved hydrogen gas was shorter than the ORP increasing time signifying a reducibility decrement; however, it is adequate to explain the reduction in of dissolved hydrogen related to the disappearing reducibility of ERW. Dissolved hydrogen was measured for only 12 hrs because the hydrogen detector used in this study cannot detect the dissolved hydrogen of a sub-ppb concentration. The comparison of the ORP results in Fig. 2 and the hydrogen concentration of Fig. 3; consequently, the decrease of hydrogen gas dissolved in ERW could explain the diminished reducibility of ERW.

The electrochemical properties of ERW with the alkalinity and reducibility of the hydroxide ion and hydrogen gas generated during the electrolysis procedure were investigated by cyclic voltammetry. Fig. 4 (a) illustrates the cyclic voltammograms of prepared ERW measured at 3 hr intervals and with at different waiting times.

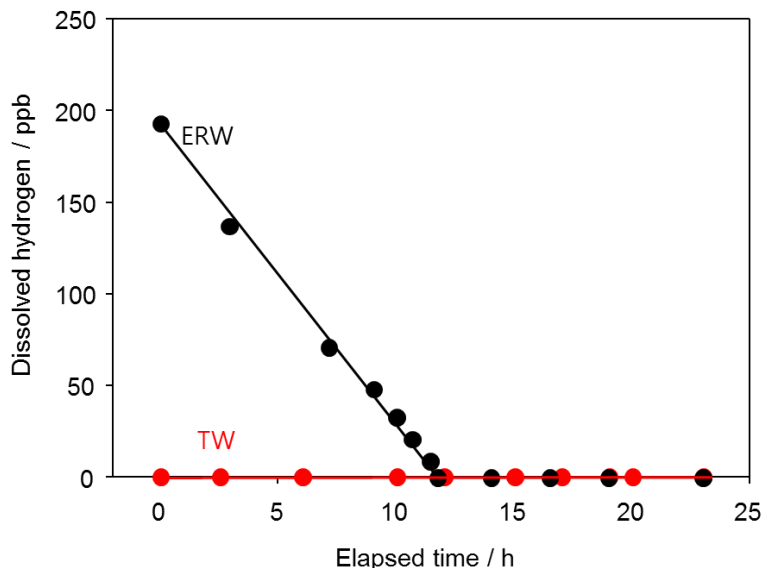


Figure 3. The variation profiles of dissolved hydrogen concentration of tap water and prepared electrolyzed reduced water as a function of waiting time.

The voltammogram of tap water was combined to compare with ERW. The cyclic voltammograms of ERW measured at different waiting times represent similar curves; however, the redox curves obtained in negative potential range (-1.1 V ~ 0.0 V) gradually shifted to the direction of lower current density as time passes. Fig. 4(a) shows the cyclic voltammograms of the electrochemical double layer measured at 0 V ~ 0.7 V potential ranges showed similar results. Fig. 4(b) shows a gradual decrement of the oxidation peaks of ERW measured as a function of time elapsing in the 0.70 V ~ 1.05 V potential range.

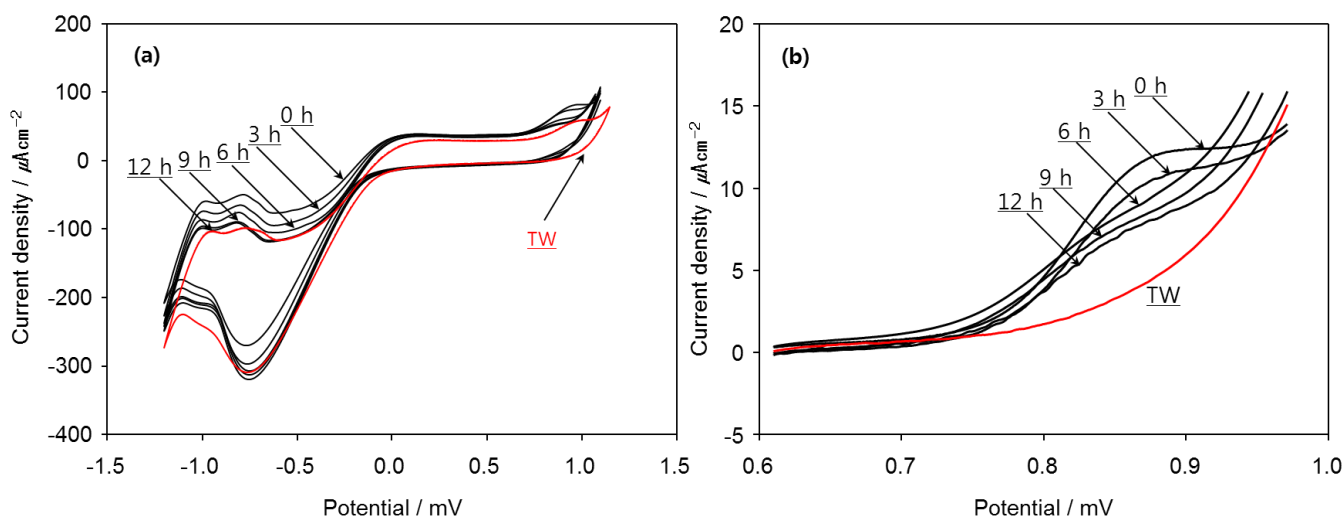


Figure 4. The cyclic voltammograms of tap water and prepared electrolyzed reduced water as a function of waiting time (a) and expanded oxidation voltammograms measured at 0.6 V – 1.0 V potential range (b).

The oxidation peak of this potential range represent a oxidation of residual hydroxide ion(OH⁻) in aqueous solution. The decrement of oxidation peak during the waiting time explains the decrement of alkaline hydroxide ion. This decrease of hydroxide ion(OH⁻) produced in a cathode chamber provided also from pH measurements. The cyclic voltammograms measured from the ERW which waiting over 9 hrs show a similar curve to tap water drawn at a lower current density range against a negative potential range. The redox properties of ERW diminished gradually by the decrement of hydrogen gas and hydroxide ion; consequently, the redox properties of ERW are similar to tap water.

Reducible hydrogen dissolved in ERW could be detected by the intentional oxidation method of hydrogen using electrochemical analysis. Dissolved hydrogen was detected by square wave voltammetry, since cyclic voltammetry cannot detect a low concentration of dissolved hydrogen in ERW. The oxidation potential of dissolved hydrogen was determined as a square wave voltammogram of hydrogen injected tap water (BHW) and identified dissolved hydrogen for ERW and purified tap water (see Fig. 5). In the potential range of 180 mV ~ 230 mV, the shoulder indicating dissolved hydrogen was identified from the square wave voltammogram of ERW and a more definite shoulder was shown by hydrogen injected tap water. Purified tap water without dissolved hydrogen showed a smooth curve without shoulder grown at the oxidation potential range of hydrogen. From the result of square wave voltammogram, the hydrogen dissolved in ERW generated by electrolysis was detected by an electrochemical method.

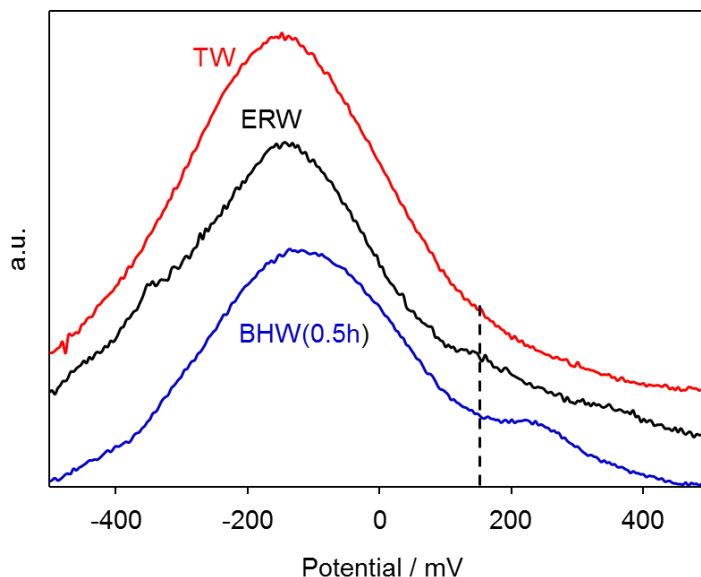


Figure 5. The square wave voltammograms of tap water, as-prepared electrolyzed reduced water and hydrogen injected tap water.

ORP signify the redox potential of an aqueous solution and measure the reducibility strength of dissolved hydrogen, but are inadequate to discuss the quantitative reducibility of ERW. A galvanostatic experiment to oxidize a reducible chemical species contained in ERW was performed to measure the reducible properties of ERW by electrochemical quantitative analysis. The stable linear

potential obtained at constant current continued during the oxidation of reducible chemical species contained in ERW and the potential increased markedly after the oxidation of all reducible chemicals dissolved in ERW. The reducible quantity of ERW could be determined as a conversion of the charging quantity into the oxidation period which obtained the EWR potential profile. Figure 6 represent each galvanostatic oxidation curve of the ERW left for 20 hrs, of the as-prepared ERW and purified tap water. As soon as the galvanostatic oxidation started, the potential response curves of the purified tap water and ERW leaving for 20 hrs increased over 0.8 V quickly. The potential response curves of as-prepared ERW extended horizontally as a function of the capacity of reduction charge and then increased over 0.8 V after 0.027 C charging. The galvanostatic oxidation also measured the generated reducibility of as-prepared ERW and explained the decreased reducibility during the leaving as shown in the ORP measurement results and the dissolved hydrogen concentration measurements. The results show that the electrochemical analysis could investigate the reducibility quantity of ERW and the available duration of the reducible ERW. This electrochemical result also explains the reducibility of ERW related to reducible hydrogen gas generated in electrolysis.

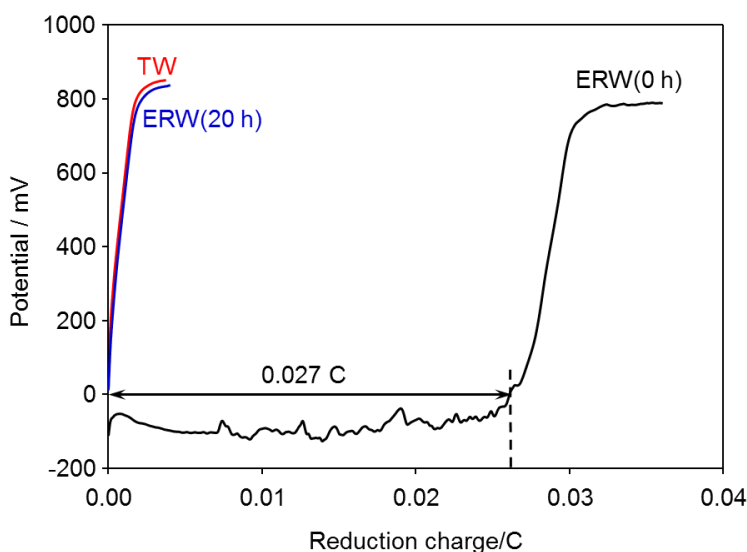


Figure 6. The galvanostatic oxidation curves of tap water, as-prepared electrolyzed reduced water and electrolyzed reduced water waiting for 20 hrs.

4. CONCLUSIONS

The reducibility and persistency against waiting time of ERW produced by purified tap water were investigated by the measurement of pH, ORP and hydrogen concentration. Cyclic voltammetry, square wave voltammetry and galvanostatic oxidation were performed for the detailed electrochemical analysis.

The alkalinity of ERW produced by purified tap water was investigated by pH measurement and the pH persistency of alkaline ERW was explained by the pH plotted profile as a function of waiting time. The high pH alkalinity of as-prepared ERW was caused by hydroxide ions produced by

an electrolysis mechanism and it became neutral tap water that gradually lost the hydroxide ions(OH⁻) over time. The relation of measured ORP and dissolved hydrogen concentration against waiting time was discussed simultaneously to analyze the core chemical species of reducibility and investigate the ORP persistency of ERW. The changed reducibility against waiting time of the ERW was explained by the change of ORP value and hydrogen concentration of as-prepared ERW. Cyclic voltammetry applied as an electrochemical analysis shows that hydroxide ions produced by cathodic electrolysis decreased as a function of waiting time. The dissolved hydrogen of low concentration was undetected by cyclic voltammetry but detected in square wave voltammetry. Electrochemical measurements using galvanostatic oxidation evaluated a reducibility magnitude of as-prepared ERW and the electrochemical reductive energy of 0.027 C was measured.

References

1. C. Kim, Y.-C. Hung and R. E. Brackett, *Int. J. Food Microbiology*, 61 (2000) 199.
2. M.A. Deza, M. Araujo and M.J. Garrido, *Lett. Appl. Microbiology*, 40 (2005) 341.
3. Y. Nagamatsu, K.-K. Chen, K. Tajima, H. Kakigawa and Y. Kozono, *Dental Materials J.*, 21 (2002) 93.
4. K. Hanaoka, D. Sun, R. Lawrence, Y. Kamitani and G. Fernandes, *Biophysical Chem.*, 107 (2004) 71.
5. Y. Tanaka, S. Uchinashi, Y. Saihara, K. Kikuchi, T. Okaya and Z. Ogumi, *Electrochimica Acta*, 48 (2003) 4013.
6. K. S. Venkitanarayanan, G. O. Ezeike, Y.-C. Hung and M. P. Doyle, *Appl. Environ. Microbiology*, 65 (1999) 4276.
7. K. Kikuchi, H. Takeda, B. Rabolt, T. Okaya, Z. Ogumi, Y. Saihara and H. Noguchi, *J. Electroanal. Chem.*, 506 (2001) 22.
8. J. Hao, Wuyundalai, H. Liu, T. Chen, Y. Zhou, Y.-C. Su and L. Li, *J. Food Sci.*, 76 (2011) C520.
9. K. Ryoo, B. Kang and O. Sumita, *J. Mater. Res.*, 17 (2002) 1298.
10. T. Takenouchi, S.-I. Wakabayashi, *J. Appl. Electrochem.*, 36 (2006) 1127.
11. S. Shirahata, S. Kabayama, M. Nakano, T. Miura, K. Kusumoto, M. Gotoh, H. Hayashi, K. Otsubo, S. Morisawa and Y. Katakura, *Biochem. Biophys. Res. Commun.*, 234 (1997) 269.
12. M. Y. Lee, Y. K. Kim, K. K. Ryoo, Y. B. Lee and E. J. Park, *Appl. Biochem. Biotechnol.*, 135 (2006) 133.
13. K.-C. Huang, C.-C. Yang, K.-T. Lee and C.-T. Chien, *Kidney International*, 64 (2003) 704.
14. M.-J. Kim, K. H. Jung, Y. K. Uhm, K.-H. Leem and H. K. Kim, *Biol. Pharm. Bull.*, 30 (2007) 234.
15. K.-C. Huang, S.-P. Hsu, C.-C. Yang, P. Ou-Yang, K.-T. Lee, S. Morisawa, K. Otsubo and C.-T. Chien, *Nephrol Dial Transplant*, 25 (2010) 2730.
16. M. Koseki, Y. Tanaka, H. Noguchi and T. Nishikawa, *J. Food Sci.*, 72 (2007) S298.
17. D. G. Kim, W. Y. Kim, C. Y. Yun, D. J. Son, D. Chang, H. S. Bae, Y. H. Lee, Y. Sunwoo and K. H. Hong, *Int. J. Electrochem. Sci.*, 8 (2013) 9835.
18. N.V. Vorobjeva, *Medical Hypotheses*, 64 (2005) 543.
19. S. Kato, Y. Saitoh, K. Iwai and N. Miwa, *J. Photochem. Photobiol. B*, 106 (2012) 24.
20. K. Kikuchi, S. Nagata, Y. Tanaka, Y. Saihara and Z. Ogumi, *J. Electroanal. Chem.*, 600 (2007) 303.
21. A. J. Bard and L. R. Faulkner, *Electrochemical Methods; Fundamentals and Applications*, John Wiley & Sons, Inc.; New York, (2001)
22. N. Menek, S. Başaran, Y. Karaman, G. Ceylan, E. Ş. Tunç, *Int. J. Electrochem. Sci.*, 7 (2012) 6465.

23. S.-M. Wang, W.-Y. Su, S.-H. Cheng, *Int. J. Electrochem. Sci.*, 5 (2010) 1649.
24. C.W.M.P. Sillen, E. Barendrecht, L.J.J. Janssen and S.J.D. van Strahlen, *Int. J. Hydrogen Energy*, 7 (1982) 577.
25. G. Krenpa, B. Hakansson and P. Ekudunce, *Electrochim. Acta*, 33 (1988) 1351.

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