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Hydrogen particles and supersaturation in alkaline water from an Alkali–Ion–Water electrolyzer

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Abstract

The hydrogen content in alkaline water obtained from an electrolytic flow cell was examined by measuring the diameter distribution of hydrogen microbubbles (hydrogen particles) in electrolyzed alkaline water using the dynamic light scattering (DLS) method. The influence of electrolysis conditions on the hydrogen content and the diameter distribution of hydrogen particles were also examined. The diameter of hydrogen particles changes rapidly with elapsed time after electrolysis, indicating that hydrogen particles grow to form large particles. The distribution of the particle diameter shows two peaks. The mean diameter of hydrogen particles is distributed mainly between 20 and 300 nm. The mean diameter decreases with an increasing current density up to 0.03 A dm^{-2}. The diameter of hydrogen particles is smaller than the equilibrium diameter obtained by the concentration of dissolved hydrogen, suggesting that the electrolyzed water is a transition state from supersaturated to saturated solutions. Hydrogen exists in particles as a colloidal solution in a region of hydrogen content in electrolyzed water above 0.75 mM, which represents the saturation concentration of the dissolved hydrogen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Colloid; Dissolved hydrogen meter; DLS; Hydrogen evolution; Hydrogen particles; Supersaturation.

1. Introduction

Water from the cathode compartment of an electrolyzer has been recognized to be supersaturated with hydrogen and many papers have reported on the electrolysis of alkaline aqueous solution at a gas-evolving electrode [1–10]. Shibata measured the supersaturation of H_2 in a solution near a gas-evolving electrode by means of a current-interruption method and reported the relationship between the degree of supersaturation at the electrode surface and current density [11,12]. Vogt reported the departure diameter of bubbles at a gas-evolving electrode [6,13]. Nefedov and Matreev discussed the formation mechanism of gas-bubble nuclei in water electrolysis and the behavior of gas bubbles [14,15]. The time dependence of the increase in supersaturation at the surface of a platinum electrode was obtained as a function of current density, and a relation between the critical supersaturation and the critical radius of a gas bubble was proposed [16]. The theoretical basis of the behavior of mass transfer at gas-evolving electrodes was discussed considering the sliding bubbles, rising detached single bubbles, jumping detached coalescence bubbles, and ensembles of these types [19].

The optical measurement of bubble behavior at a hydrogen-evolution electrode under a microscope was reported by some researchers [17–22]. Darby and Haque reported that the average departure radii of hydrogen bubbles ranged from 10 to 100 μm[18]. Measurements under a microscope were limited to diameters of hydrogen bubbles not less than 10 μm.

Recently, research has clearly shown that drinking electrolyzed water from a cathode chamber of an ‘Alkaline–Ion–Water electrolyzer’ is ‘good for one’s health’, and that the hydrogen gas in the electrolyzed water

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exhibits some anti-oxidative activities [23–25]. The state of the electrolyzed water has not been discussed adequately and the state of the hydrogen in a hydrogen-supersaturated solution has not been clarified yet.

Research has not been carried out on the supersaturated hydrogen state of the electrolyzed water effused from a cathode chamber of an electrolytic cell, which has the same ability as an 'Alkaline–Ion–Water electrolyzer', a commercial electrolyzer that produces 'alkaline water' for drinking. The purpose of this study is the analysis of the supersaturated state of hydrogen in electrolyzed water.

2. Experimental

All the chemicals used were reagent grade, and water for preparing solutions was purified by deionization, distillation and filtration. An experimental electrolyzer device was constructed from a tank, two pumps, a filter having 25 nm diameter holes (Millipore), an electrolytic cell, and Teflon pipes [26]. The electrolytic cell had two electrodes and a membrane diaphragm that separated the cathode chamber from the anode chamber. The distance between the electrode and the diaphragm was 2.0 mm and the height of the chamber housing the electrolytic cell was 10 cm. The volume of the chamber was 10 cm^3. The electrodes used in the present study were the titanium electrodes electroplated with platinum (Tanak Kikinzoku) and had an area of 50 cm^2. The current density ranged from 0.01 to 0.60 A dm^{-2}. The average linear flow velocity past the electrode ranged from 0.17 to 0.50 cm s^{-1}. Nafion 117 (Du Pont) was used as a membrane diaphragm. This device has a construction similar to that of a commercial device. The solution was stored in a tank and the dissolved oxygen in the solution was purged with pure nitrogen gas by bubbling for 1 h. The solution was supplied to each electrolysis chamber through a corresponding filter, at a flow rate ranging from about 10 to 30 ml min^{-1}. As soon as the effluent exited the cathode chamber, it was introduced into the cells for measuring the diameter of the hydrogen particles and the hydrogen content. The diameter distribution of hydrogen particles was measured by dynamic light scattering (DLS) (Otsuka Electronics, Laser Particle Analyzer PAR III type) and the hydrogen content was measured by using both a dissolved hydrogen meter (DH-meter, TOA Electronics, DH-103A type) and the chemical analysis method. The hydrogen content in electrolyzed water was determined as follows [26]. A solution (50 ml) containing 3 M (3 mol dm^{-3}) sulfuric acid and 0.01 M K_2CrO_4 was poured into a glass-stoppered flask having a capacity of 300 ml, and 3 g of platinum powder was added. Oxygen inside the flask was exchanged for nitrogen by bubbling for 1 h. Effluent from the cathode chamber was poured directly into the flask and stirred for about 30 min to oxidize the hydrogen with K_2CrO_4. A portion of the solution was then titrated with iron(II) solution to determine the amount of K_2CrO_4 consumed. The hydrogen content was calculated on the basis of the decrease in K_2CrO_4.

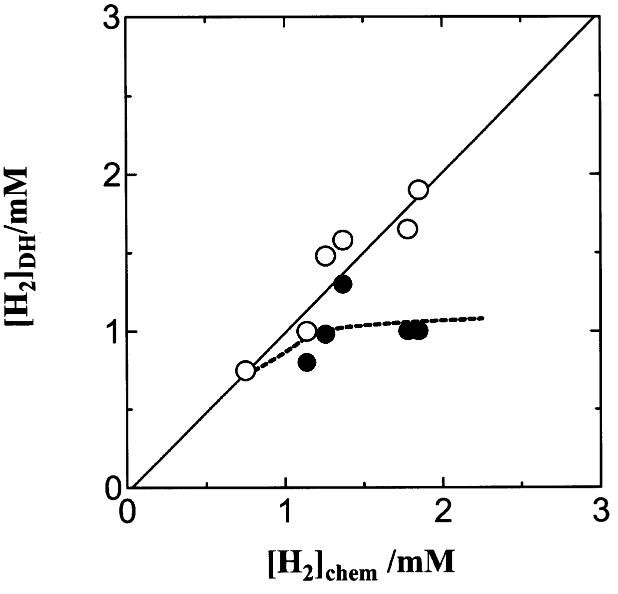

Fig. 1. Calibration curves of dissolved hydrogen concentration. ○, obtained from the five-fold diluted solutions; ●, obtained from the undiluted solution.

3. Results and discussion

The evaluation of hydrogen concentration using the chemical analysis method is outlined in Ref. [26]. The reproducibility of the values obtained from the chemical method is fairy low and the standard deviation of the analytical error was 5.0%. The detection limit of this method is about 0.05 mM hydrogen content. The chemical analysis method was found to be adequate for the purpose of the present study. Fig. 1 shows the hydrogen content of the electrolyzed water obtained by the chemical analysis method and by measurement with the DH-meter. The hydrogen content obtained from the DH-meter appears to be relatively constant, whereas the hydrogen content obtained from the chemical analysis method shows an increase. The value obtained from the DH-meter for a solution prepared with a five-fold dilution of the electrolyzed solution with pure water, is nearly the same as the value obtained from the chemical analysis method.

Fig. 2 shows the relation between the current density and the hydrogen content obtained from the chemical analysis method and the DH-meter. The hydrogen content determined by the chemical analysis method is usually greater than that determined by the DH-meter

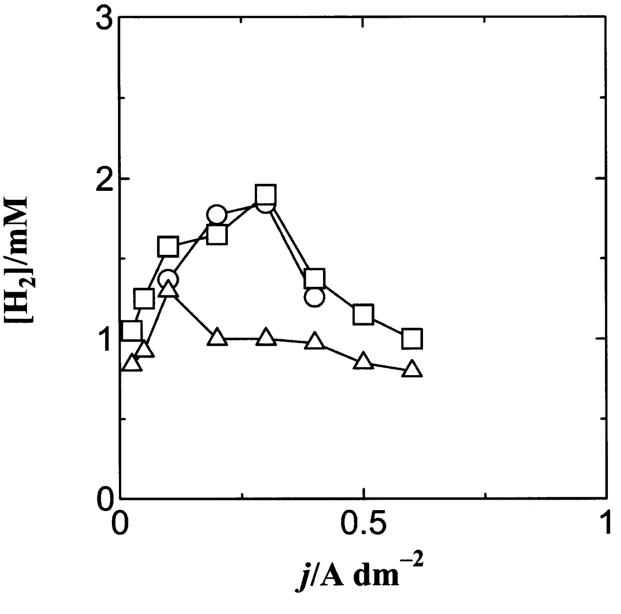

Fig. 2. Concentration of dissolved hydrogen in electrolyzed water obtained from the electrolysis of 1.70 mM NaCl solution. ○, chemical analysis; △, DH-meter; □, DH-meter (five-fold dilution).

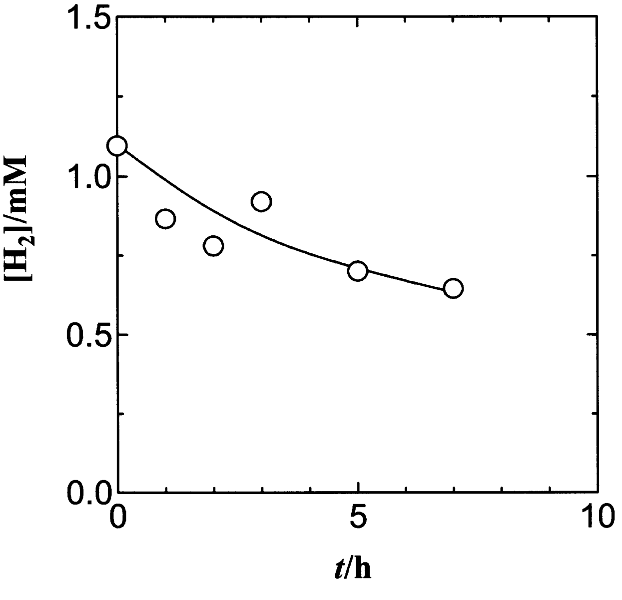

Fig. 3. Change in the dissolved hydrogen concentration with elapsed time in electrolyzed water, obtained from the electrolysis of 1.7 mM NaCl solution at 0.30 A dm^{-2}.

without dilution. However, the content obtained from the DH-meter for the five-fold diluted solution is almost the same as the content obtained from chemical analysis. The DH-meter had a membrane-type probe, and its operating principle is based on measuring a limiting current of hydrogen through a permeation membrane. Hydrogen particles, which may exist as a colloid, may not be able to diffuse directly through the membrane. Colloidal hydrogen particles may dissolve quickly into a solution when a supersaturated solution is diluted with pure water to form an unsaturated solution. Then the colloidal hydrogen particles cannot be detected as hydrogen content with the DH-meter. Therefore, the difference between the content obtained from the chemical analysis and the content from the DH-meter may be attributed to the existence of colloidal hydrogen particles, which were found to exist at current densities ranging from 0.1 to 0.4 A dm^{-2}. The hydrogen content determined by the chemical analysis method increases with current density up to 0.3 A dm^{-2} and decreases with current density beyond 0.4 A dm^{-2}. However, for a current density above 0.1 A dm^{-2}, the hydrogen content obtained from the DH-meter is almost constant at 0.95 mM. As reported by Shibata [12] and Vogt [6,13], the concentration of hydrogen at the electrode surface increases with current density up to 0.3 A dm^{-2}. At higher current density, the supply rate of the molecular hydrogen from the electrode surface becomes too rapid, the fluent formation of gaseous nuclei becomes too rigorous, and the growth rate of the hydrogen bubble becomes too high to allow stabilization of the supersaturated hydrogen solution formed at the electrode surface [13]. Therefore, the hydrogen content decreases with an increase in current density above 0.4 A dm^{-2}.

Fig. 3 shows changes in the hydrogen content with elapsed time after electrolysis. An electrolyzed solution was stored in a bottle closed tightly with a lid. The hydrogen content decreased rather rapidly after electrolysis. After 5 h, the hydrogen content decreased to the saturated concentration of 0.75 mM at 30°C.

The change in diameter of hydrogen particles with time is shown in Fig. 4. The diameter changes rather rapidly with time. Hydrogen particles in the electrolyzed solution are not very stable, making the change in diameter large. DLS measurement shows great deviation because of the low intensity of the scattering light and the large change in diameter. Subsequently, the measurement of the diameter distribution of hydrogen particles was repeated three times for electrolyzed water obtained under the same electrolysis conditions. This state may correspond to the growth of the hydrogen particles from colloidal to non-colloidal macro-bubbles, with the hydrogen particles existing for approximately 4 h in this state. The supersaturation of hydrogen was found to continue for about 4 h, which is consistent with the results shown in Fig. 3.

Fig. 5 shows a histogram of the integrated diameter distribution of hydrogen particles. The accuracy of DLS measurement below a 10 nm diameter is insufficient for discussion. Thus, we discuss the results above a 20 nm diameter. Hydrogen bubbles of 10 and 100 nm diameter yield supersaturation degrees of 210 and 21, respectively [27]. This distribution shows two peaks: the smaller peak ranges from 10 to 30 nm in diameter and

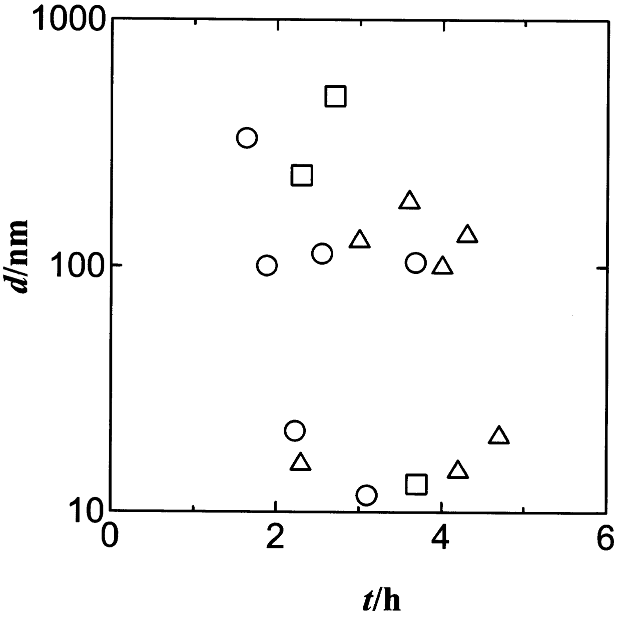

Fig. 4. Variations in the mean diameter of hydrogen particles with elapsed time. ○, 1.70 mM NaCl, 0.3 A dm^{-2}; △, 0.57 mM CaCl$_2$, 0.6 A dm^{-2}; □, 1.70 mM NaNO$_3$, 0.60 A dm^{-2}.

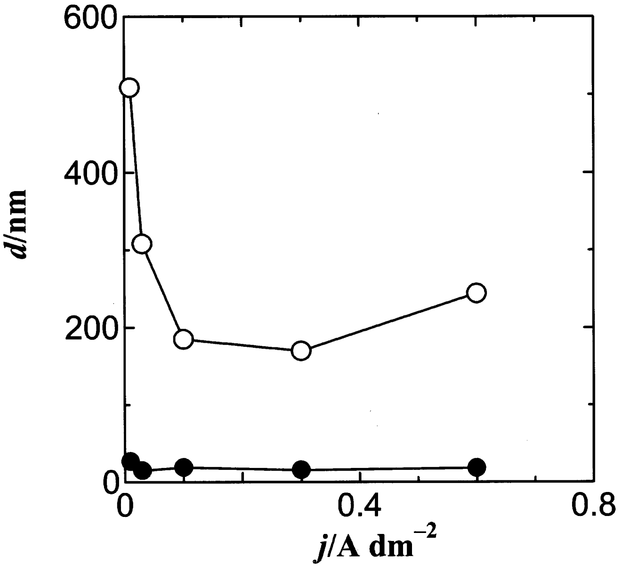

Fig. 6. Relation between the current density and the mean diameter of hydrogen particles in electrolyzed water obtained by the electrolysis of 1.70 mM NaCl solution filtered through 25 nm pores.

the larger peak from 100 to 1000 nm in diameter. Vogt reported the relation between the diameter of a hydrogen bubble and the degree of supersaturation of hydrogen, which was obtained from the ratio of hydrogen concentration to saturated hydrogen concentration, 0.75 mM [6,13]. This indicates that the hydrogen particles are smaller than the equilibrium diameter obtained from the bulk concentration of dissolved hydrogen and that the electrolyzed water is a transitional state from supersaturated to saturated solution. The growth rate of the hydrogen particles is found to be low, as the supersaturation state of the electrolyzed solution continues for about 4 h. Hydrogen particles greater than 1000 nm are excluded from the distribution, as the difference between the density of the hydrogen particles and that of a solution is too large for the hydrogen particle to stay in solution.

Fig. 6 shows the relation between the current density and the mean diameter of the hydrogen particles. The mean diameter was obtained from an integrated distribution of particle diameter. The mean diameter de-

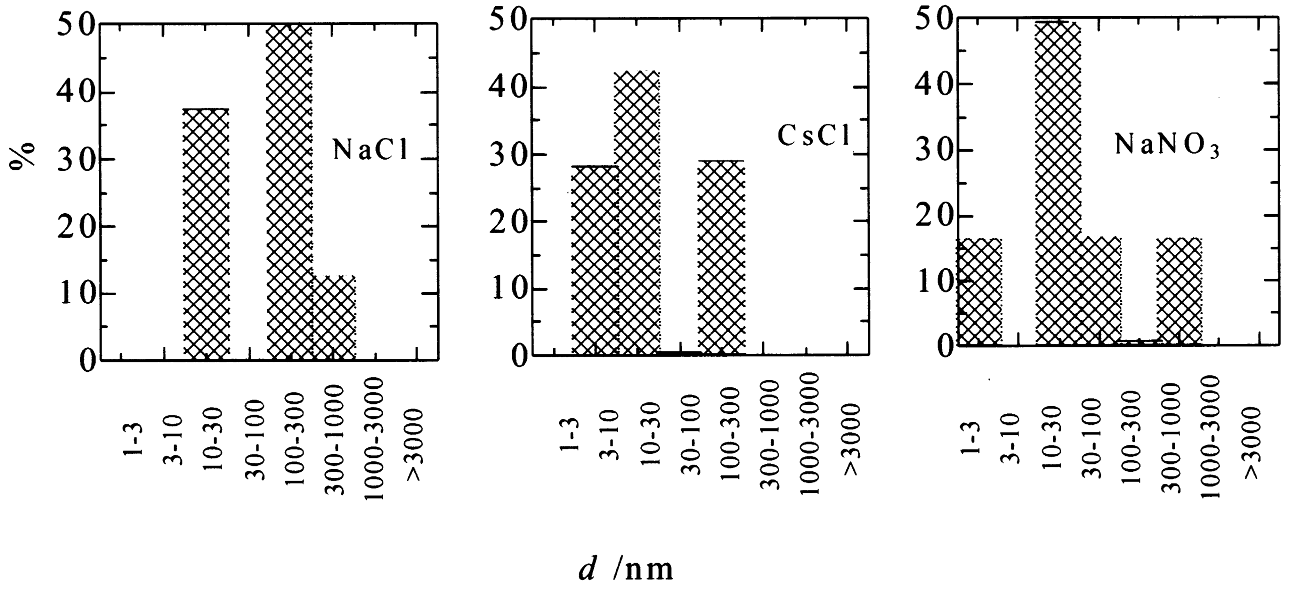

Fig. 5. Histograms obtained from an integrated diameter distribution of hydrogen particles in electrolyzed water obtained through electrolysis. Ionic strength is 1.70 mM.

creases from 510 to 185 nm with an increase in current density from 0.01 to 0.3 A dm^{-2}, followed by a weak increase at 0.6 A dm^{-2}. Vogt reported that the departure diameter of hydrogen particles at the surface of an electrode decreases with an increase in the hydrogen concentration at the surface of the electrode [13]. Therefore, these phenomena correspond to the changes in the hydrogen concentration at the surface of the electrode. Hydrogen particles may be supplied mainly in the vicinity of the surface of the electrode and at the surface of the electrode, because the degree of supersaturation in a bulk solution cannot yield hydrogen particles of diameter below 1000 nm. The growth rate of the hydrogen particles is low, because the supersaturation of the electrolyzed water continues for about 4 h. Therefore, the diameter of the hydrogen particles in an electrolyzed solution decreases with an increase in current density.

Fig. 7 indicates the relation between the current density and the mean diameter of hydrogen particles obtained by a filter having 250 nm pores instead of 25 nm pores. In the case of 250 nm pores the diameter is independent of the current density and ranges from 150 to 300 nm. A solution filtered through a filter having 250 nm pores might contain solid impurities smaller than the diameter of 250 nm. Therefore, the effects of solid impurities would mask the effects of the current density. Comparing the results of Fig. 6 with those of Fig. 7, it is found that the relationship between the mean diameter of the hydrogen particles and electrolysis conditions can be obtained only in the case of the 25 nm pore filter.

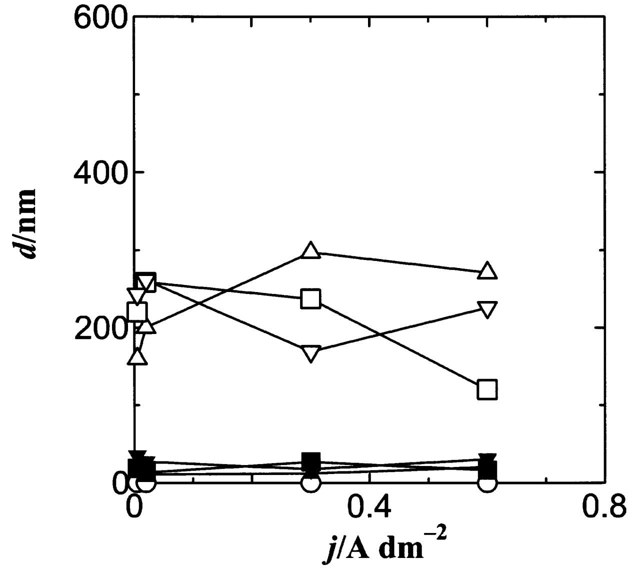

Fig. 7. Relation between the current density and the mean diameter of hydrogen particles in electrolyzed water obtained from electrolysis of a solution filtered through 250 nm pores. Concentration of NaCl (mM): ○, 0.43; △ and ▲, 1.70; □ and ■, 17.0; ▽ and ▼, 170.

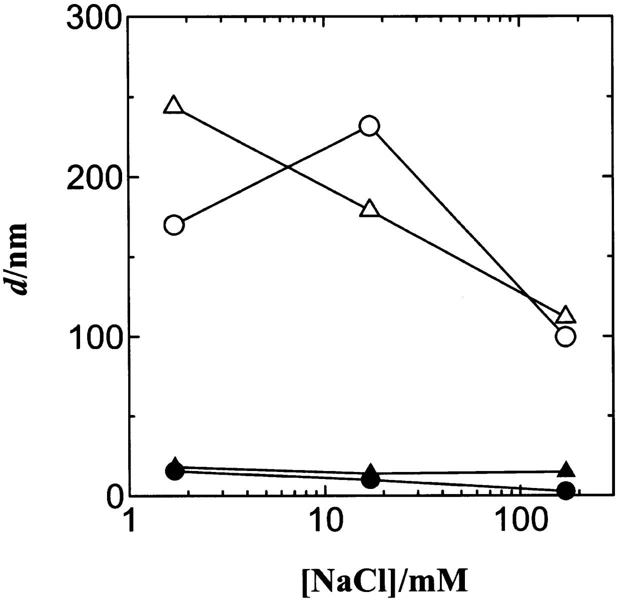

Fig. 8. The effect of NaCl concentration on the mean diameter of hydrogen particles. Current density of electrolysis (A dm^{-2}): ○ and ●, 0.3; △ and ▲, 0.6.

The effect of sodium chloride concentration on the mean diameter of the hydrogen particles is shown in Fig. 8. The diameter decreases with an increasing sodium chloride concentration, showing that particles with large mean diameter become unstable in higher concentrations of the sodium chloride solution. This phenomenon is consistent with the stability of a colloid in an electrolytic solution.

The effects of cations and anions on the mean diameter of the hydrogen particles were examined. The differences in the mean diameter among cations and anions were found to fall within the experimental error and are too small to be discussed.

4. Conclusion

The existence of hydrogen particles as a colloid in electrolyzed water was elucidated both by the DLS method and by the two methods used for determining the hydrogen content. The difference between the hydrogen content obtained from the chemical analysis method and that obtained from the DH-meter is owing to the existence of hydrogen particles. Hydrogen particles whose diameters are below about 600 nm exist as a colloid. The diameter of hydrogen particles decreased with an increasing current density and an increasing sodium chloride concentration.

References

[1] Y. Choquette, H. Menard, L. Brossard, Int. J. Hydrogen Energy 15 (1990) 21.

[2] L. Bai, D.A. Harrington, B.E. Conway, Electrochim. Acta 32 (1987) 1713.

[3] J.Y. Hout, M.L. Trudeau, R. Schulz, J. Electrochem. Soc. 138 (1991) 1316.

[4] H. Riegel, J. Mitronic, K. Stephan, J. Appl. Electrochem. 28 (1998) 10.

[5] G. Bendrich, W. Seiler, H. Vogt, Int. J. Heat Mass Transfer 29 (1986) 1741.

[6] H. Vogt, Electrochim. Acta 32 (1987) 633.

[7] L.J.J. Janssen, J. Appl. Electrochem. 17 (1987) 1177.

[8] L.J.J. Janssen, Electrochim. Acta 23 (1978) 81.

[9] L.J.J. Janssen, E. Barendrecht, Electrochim. Acta 29 (1984) 1207.

[10] G. Kreysa, B. Hakansson, P. Ekdunge, Electrochim. Acta 33 (1988) 1351.

[11] S. Shibata, Bull. Chem. Soc. Jpn. 36 (1963) 53.

[12] S. Shibata, Electrochim. Acta 23 (1978) 619.

[13] H. Vogt, Electrochim. Acta 34 (1989) 1429.

[14] V.G. Nefedov, Russ. J. Electrochem. 30 (1994) 1429.

[15] V.G. Nefedov, V.V. Matveev, Russ. J. Electrochem. 30 (1994) 1264.

[16] L. Muller, B. Schultz, Z. Phys. Chem. (Leipzig) 270 (1989) 721.

[17] L.J.J. Janssen, Electrochim. Acta 34 (1989) 161.

[18] R. Darby, M.S. Haque, Chem. Eng. Sci. 28 (1973) 1129.

[19] L.J.J. Janssen, C.W.M.P. Sillen, E. Barendrecht, S.J.D. van Stralen, Electrochim. Acta 29 (1984) 633.

[20] C.W.M.P. Sillen, E. Barendrecht, L.J.J. Janssen, S.J.D. van Stralen, Int. J. Hydrogen Energy 7 (1982) 577.

[21] N.K. Khosla, S. Venkatachalam, P. Somasundaran, J. Appl. Electrochem. 21 (1991) 986.

[22] P. Boissonneau, P. Byrne, J. Appl. Electrochem. 30 (2000) 767.

[23] K. Miyashita, M. Yasuda, T. Ota, T. Suzuki, Biosci. Biotechnol. Biochem. 63 (1999) 421.

[24] S. Shirahata, S. Kabayama, M. Miura, K. Kusumoto, Y. Katakura, Biochem. Biophys. Res. Commun. 234 (1997) 269.

[25] S. Suzuki, M. Nishina, T. Kuramochi, Y. Yamakawa, K. Yabe, M. Suzuki, Med. Biol. 131 (1995) 281.

[26] K. Kikuchi, H. Hiroko, B. Rabolt, T. Okaya, Z. Ogumi, Y. Saihara, H. Noguchi, in preparation.

[27] W.J. Moore, Physical Chemistry, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1972 (Ch. 11).