Topic Number: 17

Rate equation analysis of ROS/RNS in plasma-treated water

K. Takahashi[1], S. Kawaguchi[1], K. Satoh[1], H. Kawaguchi[1],
I. Timoshkin[2], M. Given[2], and S. MacGregor[2]

[1] *Muroran Institute of Technology, Muroran, Japan*
[2] *University of Strathclyde, Glasgow, UK*

The concentrations of H_2O_2, NO_2^-, and NO_3^- as reactive oxygen species and reactive nitrogen species in water, exposed to a pulsed discharge in nitrogen atmosphere, are calculated using rate equations coupled with acid-base equilibrium between NO_2^- and HNO_2 and a chemical reaction between H_2O_2 and HNO_2, considering the temporal variations of flux rates of H_2O_2, NO_2^-, and NO_3^-, which is estimated from measurement data in our previous work. Furthermore, the calculated concentrations are fitted to the measurement values. It is found that the calculated concentrations are in approximate agreement with the measured data. It is also found that the generation rates of H_2O_2, NO_2^- and NO_3^- are estimated to be 9.5×10^{-7}, 4.5×10^{-7}, and 2.5×10^{-7} M/s.

1. Introduction

In recent years, plasma-treated water, in which reactive oxygen species and reactive nitrogen species (ROS/RNS) dissolve, has gained increasing attention, because ROS/RNS in the plasma-treated water, such as H_2O_2 (hydrogen peroxide), NO_2^- (nitrite ion), HOONO (peroxynitrous acid), and NO_3^- (nitrate ion), and/or synergistic effects between these species play a key role in various applications such as disinfection [1] and plant growth promoting [2]. To selectively and/or effectively produce the ROS/RNS and utilize the plasma-treated water effectively and efficiently, it is important to clarify the generation process of the ROS/RNS; however, the generation process has not yet been clarified. In this work, we calculated the ROS/RNS concentrations in water, exposed to a pulsed discharge in nitrogen atmosphere, by solving rate equations coupled with acid-base equilibrium, and fitted the results to measurement values in our previous work [3].

2. Calculation methods and conditions

H_2O_2, NO_2^- and NO_3^- are produced in the water, and the pH of the water decreases with plasma exposure. NO_2^- is in acid-base equilibrium with HNO_2 (nitrous acid), and HNO_2 reacts with H_2O_2 to form NO_3^- as shown in Eq. (1) [4]; therefore, the concentrations of H_2O_2, NO_2^-, NO_3^-, and HNO_2 as functions of time t are expressed by rate equations as shown in Eqs. (2)-(7).

$$H_2O_2 + HNO_2 + H^+ \rightarrow NO_3^- + H_2O + 2H^+ \tag{1}$$

$$\frac{\mathrm{d}[H_2O_2]}{\mathrm{d}t} = F(t)G_{H_2O_2} - k[H_2O_2][HNO_2][H^+] \tag{2}$$

$$\frac{\mathrm{d}[NO_2^-]}{\mathrm{d}t} = F(t)G_{NO_2^-} \tag{3}$$

$$\frac{\mathrm{d}[NO_3^-]}{\mathrm{d}t} = F(t)G_{NO_3^-} + k[H_2O_2][HNO_2][H^+] \tag{4}$$

$$\frac{\mathrm{d}[HNO_2]}{\mathrm{d}t} = -k[H_2O_2][HNO_2][H^+] \tag{5}$$

$$[NO_2^-] = f_{NO_2^-}([NO_2^-]+[HNO_2]) \tag{6}$$

$$[HNO_2] = f_{HNO_2}([NO_2^-]+[HNO_2]) \tag{7}$$

Here, [M], $F(t)$, G_M, k, and f_M represent the concentration of product M, the time variation of flux, the generation rate of product M, rate constant, and the abundance ratio of product M, respectively. The time variation of flux is estimated from the differential coefficient of the measured concentration variations of NO_2^- and NO_3^-, and the abundance ratio is calculated from the pH of water, which is the measured data. The concentrations of H_2O_2, NO_2^-, and NO_3^- are calculated using the 4th order Runge-Kutta method, and fitted to the measurement values by varying G_M and k.

3. Results and discussion

The calculated concentrations of H_2O_2, NO_2^- and NO_3^- as functions of time are in approximate agreement with the measurement values. Therefore, NO_2^- is converted into HNO_2 under acidic conditions, and then HNO_2 reacts with H_2O_2 to form NO_3^-. It is found that the generation rates of H_2O_2, NO_2^- and NO_3^- for the plasma treated water are estimated to be 9.5×10^{-7}, 4.5×10^{-7}, and 2.5×10^{-7} M/s.

4. References

[1] A. Kojtari, T.K. Ercan, J. Smith, G. Friedman, R.B. Sensenig, S. Tyagi, S.G. Joshi, H-F. Ji, and A.D. Brooks, J. Nanomed. Biother. Discov. **4** (2013) 120.
[2] K. Takaki, J. HTSJ, **51** (2012) 64.
[3] K. Takahashi, K. Satoh, H. Itoh, H. Kawaguchi, I. Timoshkin, M. Given, and S. MacGregor, Jpn. J. Appl. Phys. **55** (2016) 07LF01.
[4] G. Merényi, J. Lind, G. Czapski, and S. Goldstein, Inorg. Chem. **42** (2003) 3796.