Synthesis of Peracetic Acid and Determination

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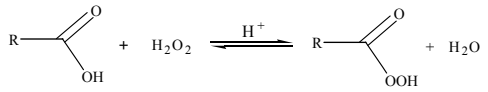
Abstract-The preparation of peroxyacetic acid (PAA) using acetic acid and hydrogen peroxide (H_2O_2) in the presence of perfluorinated resinsufonic acid (Nafion-H) in room temperature has been studied. The prepared PAA is determinate with Au electrode by cyclic voltammograms of after background subtraction. A form reaction of PAA is reach equilibrium at reaction time was around 6 hours. The concentration of PAA solution prepared was increased with the reaction time and longer reaction time it was almost constant (ca. 4.0 mmol/L).

Key words-Peroxyacetic Acid; Synthesis; Nafion – H; Determination

Ⅰ. INTRODUCTION

In recent years, peracetic acid (PAA) has been widely used as a disinfectant in the food and as a bleaching agent for textile and paper [1-3]. Preparation of PAA is generally based on a reversible chemical reaction between hydrogen peroxide (H_2O_2) and lower aliphatic carboxylic acid (eq.1) under the catalysis of a strong acid, e.g., sulfuric acid. The reaction proceed with a rate constant dependent of the concentration of catalytic acid and temperature [4].



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However, this technique suffers from the drawbacks such as separation of soluble catalyst from the reaction mixture and corrosion of the reactor. Solid superacids have been used effectively in various acid-catalyzed reactions in place of the conventional acid catalysts because of their higher catalytic activity, minimal corrosion problems, ease of separation and reusability [5, 6]. Now we wish to report the preparation of PAA using acetic acid and H_2O_2 in presence of the solid superacid, Nafion-H (a solid perfluorinated resinsulfonic acid) in room temperature. For the first time, the prepared PAA is determinate with gold electrode by cyclic voltammograms of after background subtraction.

Ⅱ. EXPERIMENTAL

A. Preparation of PAA. Quantitative 31% H_2O_2 and Nafion resins add to 1mol/L acetic acid solution. Agitate by stir in room temperature. All solutions were prepared using deionized water.

B. Determination of PAA. The Au working electrodes were polished with emery paper and aqueous slurries of finer aluminium power (1 μm and 0.06 μm) successively. Then they were sonicated in water for 5 min, and electropolished in 0.05 mol/L H_2SO_4 solution for about 10 min before the typical cyclic voltammogram was taken. The platinum wire and NaCl-saturated Ag/AgCl electrode were used as counter and reference electrode (Figure 1).

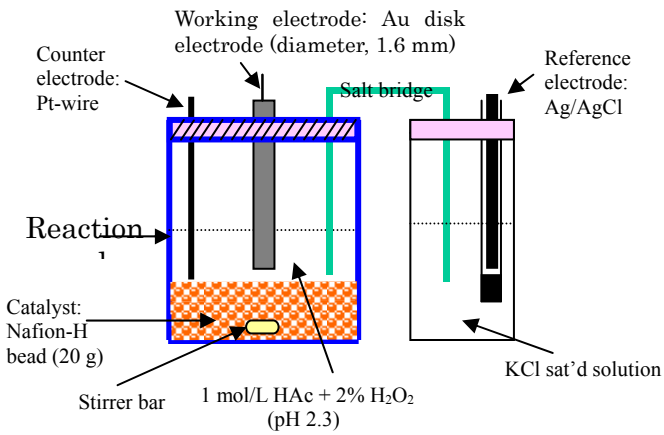

Figure 1 Reaction Scheme for PAA Synthesis.

C. Regeneration of Nafion-H Catalyst. Treated in boiling deionized water for 2 h and then filtered. The resin is then stirred in 20% HNO_3 for 4-5 h at room temperature and filtered. This acid treatment is repeated three to four times to obtain maximum exchange of potassium ion with protons in the polymer. The resin is finally washed several times with water until a neutral filtrate is obtained followed by drying under vacuum at ~ 105°C for at least 24 h.

Ⅲ. RESULTS AND DISCUSSION

Figure.2 shows cyclic voltammetric behaviors of PAA and H_2O_2 obtained at Au electrode in N_2-saturated 1 mol/L acetic acid solution. We can see two well-separated reduction peaks or the reduction of PAA and H_2O_2, respectively. This can be easily noticed from the increase in the intensity of the two peaks with the increase in the concentration of PAA and H_2O_2 (curves b, c, and d), from the increase in the peak intensity only at -0.4V on keeping the concentration of PAA constant, while increasing that of H_2O_2 (curves d, e, and f). It follows from what has been said that PAA can be examined in acetic acid

solution. The question, which we must consider, next is influence of oxygen.

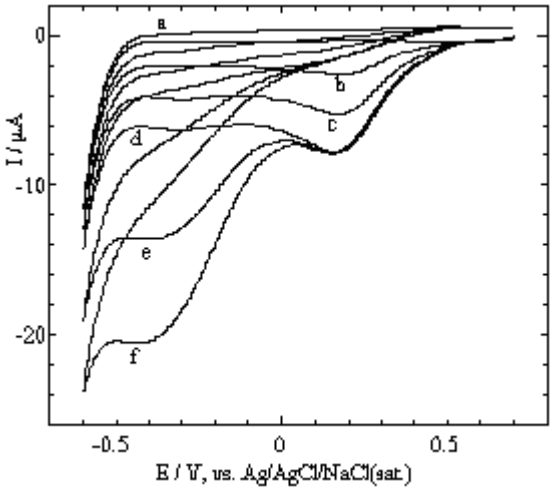

Figure 2 Cyclic voltammograms obtained for the PAA and H_2O_2 at Au electrode (ϕ = 1.6 mm) in N_2-saturated 1mol/L CH_3COOH solution (pH = 2.3). Potential scan rate: 100mV/s. (a) blank.
(b) 0.275 mmol/L PAA + 0.092 mmol/L H_2O_2.
(c) 0.55mmol/L PAA + 0.184 mmol/L H_2O_2.
(d) 0.825 mmol/L PAA + 0.276 mmol/L H_2O_2.
(e) 0.825 mmol/L PAA + 0.776 mmol/L H_2O_2.
(f) 0.825 mmol/L PAA + 1.276 mmol/L H_2O_2.

Figure.3 shows cyclic voltammograms of PAA reduction at Au electrode in acetic acid solutions under N_2 and air. Oxygen reduction (-0.1 V) between PAA and H_2O_2 reduction, no affect for determine of PAA. So far, we have seen how determine of PAA in acetic acid solutions, oxygen was no affect for examine of PAA.

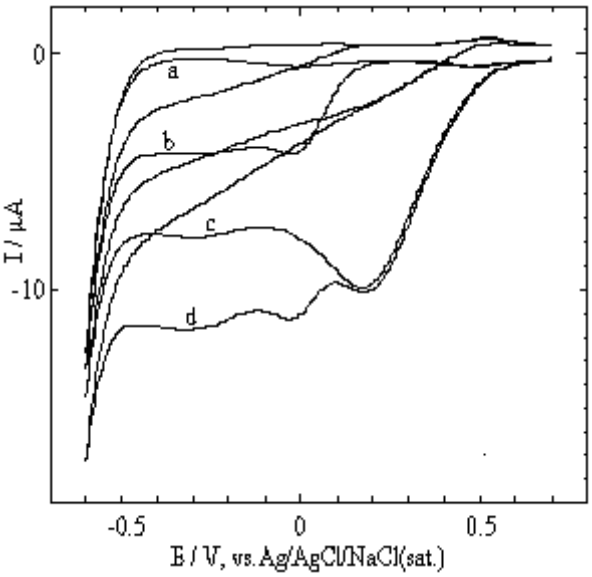

Figure 3 Cyclic voltammograms obtained at Au electrode (ϕ = 1.6 mm) in (a, c)N_2 and (b, d) air-saturated 1mol/L CH_3COOH solutions (pH = 2.3) in the absence (a, b) and presence (c, d) of 2.2 mmol/L PAA + 0.73mmol/L H_2O_2

Figure. 4 show Cyclic voltammograms obtained at Au electrode in N_2-saturated 1 mol/L CH_3COOH solution containing 2% H_2O_2. Solid and dotted lines show CVs obtained in the absence and presence of 4.4 mmol/L PAA, respectively. CV for the reduction of PAA, which was corrected by subtracting solid line CV from dotted line CV (Figure.4 inset). The concentration of PAA can be obtained, according to the standard curve of concentration of PAA to current intensity.

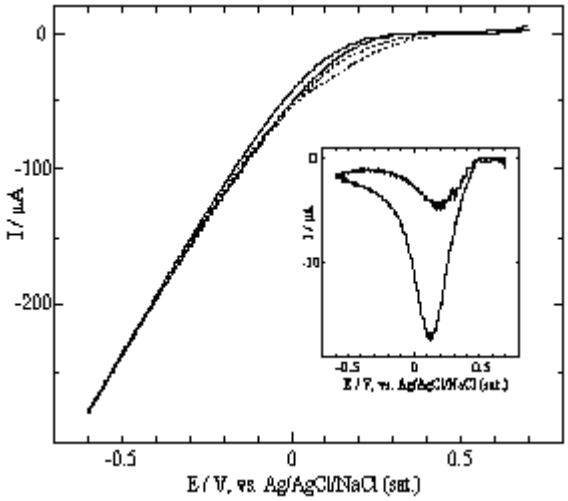

Figure 4. Cyclic voltammograms obtained at Au electrode in N_2-saturated 1 mol/L CH_3COOH solution containing 2% H_2O_2. Solid and dotted lines show CVs obtained in the absence and presence of 4.4 mmol/L PAA, respectively. Inset: CV for the reduction of PAA, which was corrected by subtracting solid line CV from dotted line CV. Potential scan rate: 100mV/s.

Figure.5 show the concentration of PAA produced by the 1 mol/L acetic acid solution (20 mL) containing 2% H_2O_2 and Nafion-H (about 20 g) in batch- wise operation as a function of the reaction time. The concentration of PAA solution prepared was increased with the reaction time and longer reaction time it was almost constant (ca. 4.0 mmol/L). A form reaction of PAA is reach equilibrium at reaction time was around 6 hours. PAA can not be obtained, in test time, without Nafion. In conclusion, we have succeeded in preparing PAA from acetic acid and hydrogen peroxide using solid superacid catalysts Nafion-H.

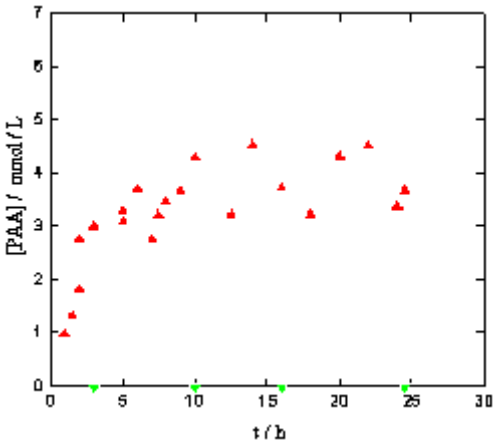

Figure 5. Plot of PAA concentration *vs.* reaction time. (▲) presence of Nafion bead, and (▼) absence of Nafion bead.

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