Preparation of Hydrogen Peroxide by Electrochemical Method

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ABSTRACT

Nowadays all of the world most of hydroxide peroxide producing at industrial scale has been using as bleaching agent of light industry product such as paper, fibre et all, and the demand on it continuously has increased. Specially, in paper industry hydroxide peroxide not only bring about a substantial improvement of the quality of paper but also has no influence upon the human body and environment, and so is widely using as bleaching agent of hypochlorite. But for serious reasons on the use such as storage and transport of hydroxide peroxide in work shop is the main trend at present.

We studied the preparation of hydrogen peroxide by a new and facile method based on cathodic reduction of oxygen with the gas diffusion type-oxygen electrode.

1. Theoretical basis of preparing hydroxide peroxide by electrochemical method

When electrolyze with the gas diffusion type-oxygen electrode as cathode, metal having a low oxygen overvoltage as anode in alkali electrolyte, the reaction as following can take place [2,3]:

cathode: $2O_2 + 2\ H_2O + 4e \rightarrow 2HO_2^- + 2OH^-$ (1)

anode : $4OH^- \rightarrow O_2 + 2H_2O + 4e$ (2)

overall reaction : $O_2 + 2OH^- \rightarrow 2HO_2^-$ (3)

On the other hand, a failure in supply of oxygen at cathode dr a gradual accumulation of HO_2^-ions can simultaneously accuse the secondary reaction as following:

cathode: $2H_2O + 4e \rightarrow H_2 + 2OH^-$ (4)

$HO_2^- + H_2O + 2e \rightarrow 3OH^-$ (5)

anode : $HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e$ (6)

Therefore, the yield of hydrogen peroxide can be raised during the sufficient supply of oxygen to cathode in the definite condition of electrolysis.

2. Experimental consideration for preparing hydrogen peroxide by electrochemical method experimental

The electrochemical device for preparation of hydroxide peroxide was composed as shown in Fig.1.

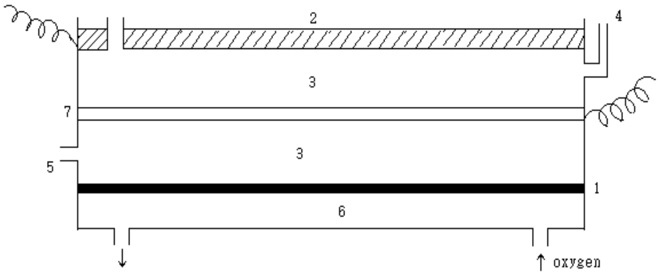


Fig.1 Schematic of device for preparation of hydroxide peroxide.

1- Cathode, 2- anode, 3- electrolyte, 4- electrolyte inlet, 5- electrolyte outlet, 6- oxygen chamber, 7- separator

In the experiment stainless steel plate(170×100×1.0 mm)was used as anode, the gas diffusion type-oxygen electrode prepared by method described in reference [1] as cathode. And sodium hydroxide wide a definite concentration added EDTA as addition agent was used as electrolyte, a perforated plate of emulsified polyvinyl chloride with a thickness of 0.48 mm and porosity of 45% as separator.

We have made an experiment in constant current condition at room temperature while sufficient supply oxygen to cathode chamber. The polarization characteristic of electrode was measured by method indicated in reference [1] compare with zinc electrode and the concentration of hydrogen peroxide in electrolyte was decided with potassium permanganate titrimetry.

Result and discussion

1) Cathodic polarization characteristic of electrolytic process

The experiments were perfomed in 1mol/L NaOH solution at room temperature, the cathodic polarization characteristic is shown in Fig.2.

As shown in Fig.2, cathodic polarization of electrolytic process satisfied for Tafel equation. This shows that when electrolyze in 1mol/L NaOH solution at room temperature, anodic polarization of electrolytic process at more lower interval than current density of 20 mA/cm² put on electrochemical kinematics region.

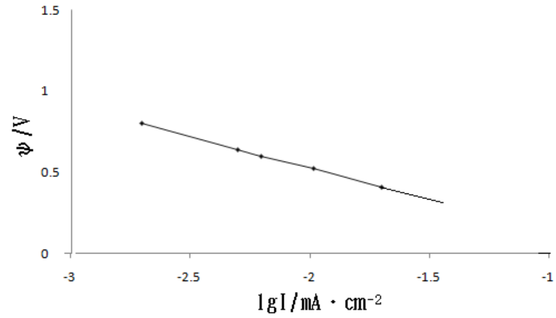


Fig.2 Cathodic polarization curve of electrolytic process

2) Effect of some electrolysis condition upon production concentration of hydrogen peroxide

Effect of current density

When electrolyze in 1mol/L NaOH solution containing an added EDTA of 0.05% for 180min, the concentration change of produced hydrogen peroxide increasing with current density showns in Fig.3.

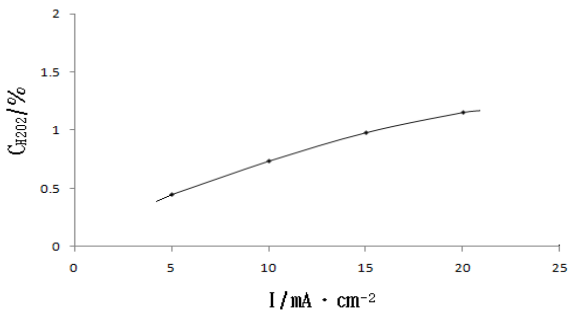


Fig.3 Concentration change of hydrogen peroxide increasing with current density

As shown in Fig.3, the concentration of produced hydrogen proxide increased with increasing current density. This explains that the higher increase current density, the denser can produce hydrogen peroxide. But should consider that when current density increase, cathodic potential can approache to deposition potential of hydrogen peroxide(theoretical value is 0.42V νs Zn/Zn^{2+}) and second reaction(4) occur while the inner temperature of device increase, therefore result in accelerating decomposition of hydrogen peroxide.

Effect of electrolyte concentration

When electrolyze at the current density of 15 mA/cm² for 180 min, the concentration change of hydrogen peroxide increasing with concentration of sodium hydroxide electrolyte shows in Fig.4.

As shown in Fig.4, the concentration of hydrogen peroxide increase and the increasing rate gradually decrease increasing with the concentration of sodium hydroxide. This explains that the denser concentration of electrolyte, the denser can attain hydrogen peroxide.

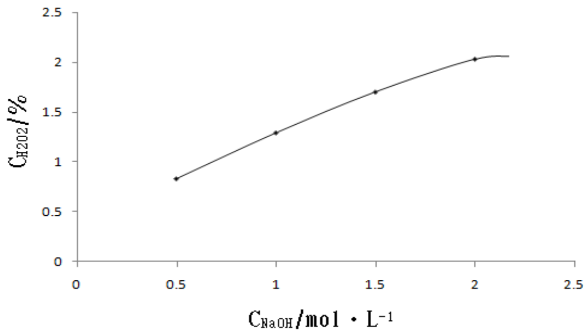


Fig.4 Concentration change of hydrogen peroxide increasing with concentration of sodium hydroxide

But we should consider that denser electrolyte concentration effects on life of the gas diffusion type-oxygen electrode and leads to increasing consumption of sodium hydroxide, therefore it is suitable to electrolyze in sodium hydroxide solution of 1mol/L.

Effect of electrolysis time

Table.1 shows the concentration change of hydrogen peroxide increasing with electrolysis time when electrolyze in 1mol/L NaOH solution at current density of 15 mA/cm^2.

As shown in Table.1, the concentration of produced hydrogen peroxide gradually increases with electrolysis time. From such electrolysis conditions and results, in view of the productivity of hydrogen peroxide, when electrolysis time set up 180min, hydrogen peroxide can be attained more than of 1.3%.

Table.1 Concentration change of hydrogen peroxide increasing with electrolysis time

Electrolysis time/min	30	60	90	120	150	180	210
Hydrogen peroxide concentration/%	0.24	0.59	0.73	0.92	1.18	1.30	1.34

Effect of impurity

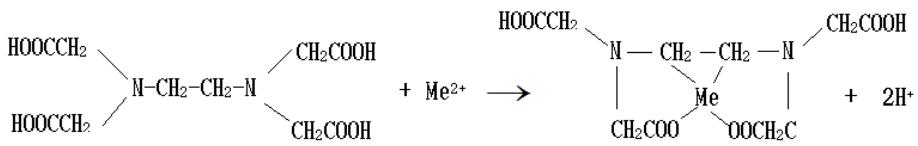
In experiment we considered the effect of impurity using the sodium hydroxide solution including a very small amount of impurity such as Fe^{2+}, Cu^{2+}, Pb^{2+} as electrolyte as compared with the pure solution. The electrolytes were prepared with industrial sodium hydroxide solution of 23.7%(d=1.26), which were diluted until 4% and added EDTA od 0.05%.

When electrolyze in the industrial and pure sodium hydroxide solution for 180min, the concentration change of produced hydrogen peroxide shows in Table.2.

Table.2 Concentration change of hydrogen peroxide increasing with current density(%)

Electrolyte kind	Current density/($mA \cdot cm^{-2}$)			
	5	10	15	20
Pure sodium hydroxide	0.36	0.83	1.30	1.45
Industrial sodium hydroxide	0.35	0.81	1.29	1.43

As shown in Table.2, for the concentration change of hydrogen peroxide increasing with current density, there are no significant differences between the two cases using the industrial and pure sodium hydroxide. It is probable reasonable to consider that impurities transition metal ions such as Fe^{2+} are decomposition catalyst of hydrogen peroxide, but the stable complex compound are formed with them by EDTA which complex-forming ability is excellent.



(7)

Therefore, the industrial sodium hydroxide including a very small amount of impurity in certain limiting extent also can be used as electrolyte for preparing hydrogen peroxide when suitable addition agents and amounts are chosen.

3) Yield of hydrogen peroxide

The yield of hydrogen peroxide based on concentration measurement result of produced hydrogen peroxide in several electrolytic conditions was calculated by the following equation.

$$\alpha = \frac{m}{m_0} \times 100 \qquad (8)$$

Here α is yield of hydrogen peroxide, m_0 is theoretic amount prepared with producing device of hydrogen peroxide and m is the amount obtained in experiment.

When electrolyze in 1mol/L NaOH solution added EDTA of 0.05% for 180min, the yield change of hydrogen peroxide increasing with current density shows in Table.3.

Table.3 Yield change of hydrogen peroxide increasing with current density

Current density/ $(mA\cdot cm^{-2})$	Production amount of hydrogen peroxide			Theoretic amount/g	α/%
	Concentration /%	Volume/mL	Pure H_2O_2 amount/g		
5	0.36	100	0.36	1.20	30.0
10	0.83	100	0.83	2.28	34.9
15	1.30	100	1.30	3.61	36.0
20	1.45	100	1.45	4.75	30.5

As shown in Table.3, the most high yield of hydrogen peroxide can be achieved in current density of 15 mA/㎠.

Conclusion

With producing device of hydrogen peroxide using cathodic reduction reaction can obtained hydrogen peroxide more than 1.3% in the following electrolysis conditions: current density of 15 mA/㎠, 1mol/L sodium hydroxide solution, electrolyte time for 180min, 20℃ electrolysis temperature. In this condition the yield of hydrogen peroxide is 36.0%.

Reference

1. Journal of KIM IL SUNG University (Natural Science), 56, 8,115, Juche99(2010)
2. B. E. Alcaide et al.; Electrochimica Acta, 48, 4, 331, 2002
3. E. B. Wayne; WO2008042662, 2008