

# ELECTROLYTIC PREPARATION OF SODIUM AND POTASSIUM PERCARBONATE

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The influence of different parameters such as current density, temperature, concentration of electrolyte and the effect of different addition agents and their composition on the electrochemical preparation of sodium and potassium percarbonate has been investigated. Optimum conditions for the preparation of these persalts are indicated.

## INTRODUCTION

Percarbonates and perborates serve as dry carriers of hydrogen peroxide, a very important chemical required on large tonnage for a variety of purposes. The largest use of the percarbonate is in household dry bleach and laundry detergent formulations. It is also used in triple bleaching and denture cleansers and as a disinfectant.

Percarbonates are peroxy compounds. Of the percarbonates, the preparation of potassium percarbonate has been mainly investigated due to the higher solubility of the potassium salt [1-6]. Higher current density, lower temperature and a smooth platinum anode are recommended. Though four compounds of sodium carbonate with hydrogen peroxide are known [7], only sodium carbonate sesqui (peroxyhydrate) is being commercially produced in USA, Europe and Japan.

The electrolytic formation of sodium percarbonate has been studied by Le Blanc and Zellmann [8]. The effect of addition of fluoride, perchlorates, sodium chloride, sodium sulphate, ferric chloride and sodium cyanide to the sodium carbonate electrolyte has been investigated [8-10].

## EXPERIMENTAL

Formation of sodium and potassium percarbonate has been studied by analysis of the electrolyte for the active oxygen that is formed over definite time intervals. The effects of variation of current density at the anode and cathode, temperature of electrolyte and concentration of electrolyte and stabiliser on the current efficiency were determined.

Smooth platinum anode which has a high oxygen over potential was used as the anode. Saturated solution of sodium carbonate was used for  $\text{Na}_2\text{C}_2\text{O}_6$  formation since it is reported to result in better efficiencies.

The electrolytic cell was a glass container of 300 ml capacity provided with a PVC cover with slots for anode, cathodes, stirrer and thermometer/sampling inlet. Smooth platinum anode (4.1 cm x 2.2 cm x 0.1 mm) and (5.2 x 4.8 cm) were kept centrally, for the sodium and potassium percarbonate respectively - flanked by two perforated stainless steel cathodes (7.1 cm x 6.1 cm) wrapped with terylene diaphragm. The interelectrode distance was 0.5 cm. 280 ml of electrolyte was taken in the cell. The electrolyte was stirred by a glass stirrer driven by a motor. The cell was surrounded by a glass trough containing ice-common salt mixture for cooling. For the potassium percarbonate electrosynthesis, a Julabo circulating cooler was used for flowing cold methanol through the jacket surrounding the cell. Direct current was supplied from a rectifier (0-30 Amp, 0-15 volts).

During electrolysis, a sample of 5 ml of solution was removed every 5 minutes for the sodium percarbonate and every 15 minutes for the potassium percarbonate for analysis. 5 ml of the original electrolyte was fed back immediately.

A total quantity of 0.5 - 2 Ah and 2 Ah of electricity was passed for each experiment done for sodium percarbonate and potassium percarbonate electrosynthesis respectively.

## Analysis

25 ml of 1 N  $\text{H}_2\text{SO}_4$  was added to 5 ml of the solution, and this solution was titrated against standard  $\text{KMnO}_4$  solution.

## RESULTS AND DISCUSSION

### Variation of Anode current density

Table I and Figure 1 give the effect of variation of anode current density on current efficiency. It is seen that a maximum current efficiency of 38.5% is obtained at medium current density 20 A/dm<sup>2</sup> for sodium percarbonate formation. Similarly for potassium percarbonate medium current density of 40 – 60 A/dm<sup>2</sup> is found to be optimum (Fig.1). Such a maximum is recorded for perborate preparation also [11,12]. Whereas higher current densities are generally needed for the formation of persalts, at still higher current densities, probably the oxygen evolution takes place and consequently current efficiency is lowered for percarbonate formation. Another reason may be the excessive heating up of the anode at higher current densities, causing heating up of the electrolyte around the anode leading to the decomposition of the product formed at it.

Fig 1: Effect of anode current density on potassium percarbonate formation

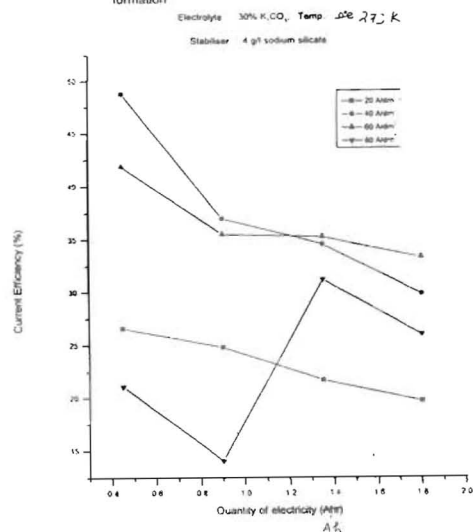


Table - I

Electrosynthesis of Sodium percarbonate- Variation of Current Density

Composition of electrolyte : Saturated solution of sodium carbonate (120 g/l)

Sodium metasilicate 3g/l

Temperature : 283K

S.No.	Anode Current density (A/dm <sup>2</sup> )	Cathode current density (A/dm <sup>2</sup> )	Voltage (V)	Current (A)	Current efficiency (%)
1.	10	2.5	4.0	1	4.6
2.	20	5.0	4.9	2	38.5
3.	40	10.0	5.6	4	35.5

### Variation of temperature

Table II for Na<sub>2</sub>C<sub>2</sub>O<sub>6</sub> and Fig.2 for K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> give the effect of variation of temperature on current efficiency. Whereas current efficiency for sodium percarbonate formation shows a maximum at 283K the potassium percarbonate shows the highest current efficiency only at the lowest temperature studied i.e. 263K. The decrease of current efficiency with increase of temperature for potassium percarbonate shows the increasing instability of the product as temperature is increased. Le Blanc and Zellmann [8] report a higher current efficiency at 273K as compared to 288K for sodium percarbonate formation. Sorokina [13] reports increase of current efficiency with temperature for K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> formation, but the range of temperature studied is not known.

Fig 2: Effect of change of temperature on potassium percarbonate formation

Anode current density : 40 A/dm<sup>2</sup>, Other conditions as in Fig 1

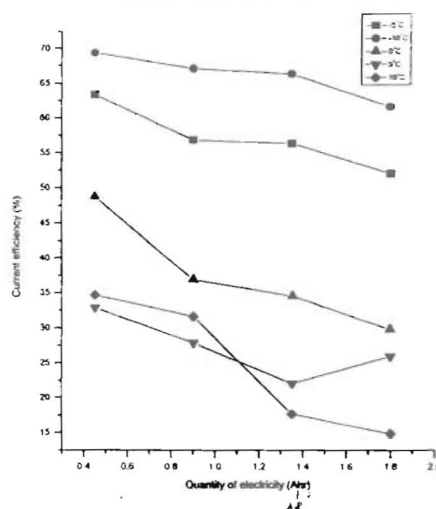


Table - II

Electrosynthesis of sodium percarbonate- Variation of Temperature

Electrolyte : Saturated solution of Na<sub>2</sub>CO<sub>3</sub>  
Na<sub>2</sub>SiO<sub>3</sub> : 3g/l

Current density : 20 A/dm<sup>2</sup> (anodic)

2.5A/dm<sup>2</sup> (cathodic)

S. No.	Temperature (K)	Voltage (V)	Saturated solution g/l (Na <sub>2</sub> CO <sub>3</sub> )	Current efficiency (%)		
				5 min	15min	30 min
1.	273	6.9	70	41.8	37.1	24.4
2.	283	4.9	120	36.2	39.3	37.1
3.	293	3.8	215	31.6	12.4	17.3



### Variation of cathode current density

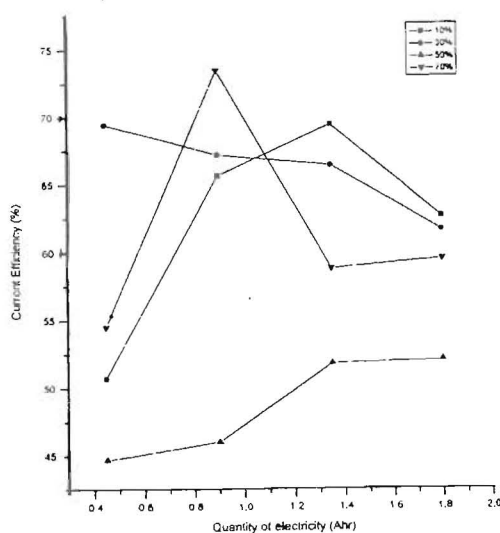
Only a slight difference in current efficiency was seen for the two cathode current densities studied ( $8 \text{ A/dm}^2$  and  $2.5 \text{ A/dm}^2$ ) (for  $\text{Na}_2\text{C}_2\text{O}_6$ ) though voltage is higher to the tune of 30% for the higher current density. It is reported that a low cathode current density is normally favoured for a persalt production [3]. Higher cathode current densities lead to hydrogen polarisation and formation of free ammonia gas on the cathode, in the persulphate preparation. For perborate preparation, the cathode current density ranges from 15 to  $20 \text{ A/dm}^2$  and should not be less than  $10 \text{ A/dm}^2$  [14].

### Variation of concentration (Fig.3)

For  $\text{Na}_2\text{C}_2\text{O}_6$ , a saturated solution of  $\text{Na}_2\text{CO}_3$  (120 g/l) has been used as electrolyte. An initial electrolyte concentration of 10–30% is seen to be optimum for  $\text{K}_2\text{C}_2\text{O}_6$ . Higher concentrations result in lower current efficiencies:

Fig. 3: Effect of change of concentration on potassium percarbonate formation

Temperature:  $-10^\circ\text{C}$ , Other conditions as in Fig 2



### Variation of addition agent and its concentration

Table III and Fig. 4 give the effect of addition agents. It is seen that sodium metasilicate at a concentration of 4 g/l gives the highest efficiency for both the percarbonates, though the cell voltage increases with increased concentration of silicate (Table III) for  $\text{Na}_2\text{C}_2\text{O}_6$ . For  $\text{K}_2\text{C}_2\text{O}_6$ , 2 g/l  $\text{Na}_2\text{SiO}_3$  gives almost the same result after passage of 1.8 Ah and there is not much change in cell voltage with different silicate concentrations. The range of concentration of the silicate studied here is higher than that studied by Khomutov et al. [15] who found that with increase of  $\text{K}_2\text{SiO}_3$  concentration (0.15–1.5 g/l) in 4M  $\text{K}_2\text{CO}_3$  current efficiency for  $\text{K}_2\text{C}_2\text{O}_6$  synthesis increases and rate constant of its thermal decomposition decreases.

Table - III

Electrosynthesis of sodium percarbonate-Variation of addition agent and its concentration

Composition of electrolyte : Saturated solution of  $\text{Na}_2\text{CO}_3$  (120g/l)+addition agent

Current density :  $20 \text{ A/dm}^2$  (anodic)

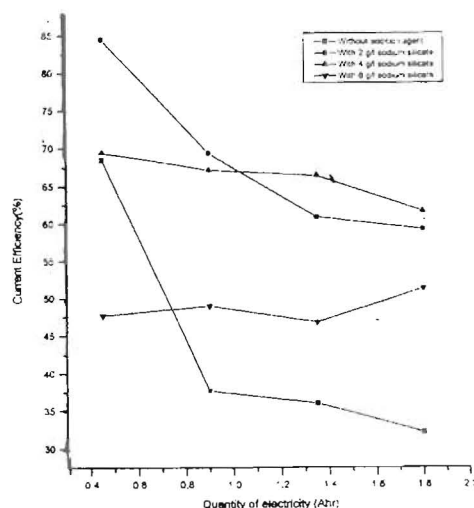
:  $2.5 \text{ A/dm}^2$  (cathodic)

Temperature : 283–285K

S. No.	Addition agent g/l	Voltage (V)	Current efficiency (%)		
			10 min.	20 min.	30 min
1	$\text{Na}_2\text{SiO}_3:2$	3.3	37.1	23.2	23.2
2	$\text{Na}_2\text{SiO}_3:3$	4.9	38.5	38.5	37.1
3	$\text{Na}_2\text{SiO}_3:4$	5.8	47.8	47.1	46.4
4	$\text{Na}_2\text{SiO}_3:5$	6.0	45.5	43.9	40.7
5	Trisodium ortho-phosphate:200	4.5	20.9	12.8	17.0
6	Trisodium ortho-phosphate+ $\text{Na}_2\text{SiO}_3$	4.6	26.9	24.5	17.2
7	Without addition agent	4.0	22.0	13.8	—

Fig.4: Effect of concentration of addition agent ( $\text{Na}_2\text{SiO}_3$ ) on potassium percarbonate formation

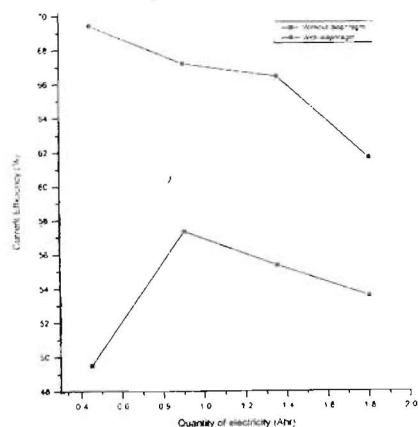
Electrolyte: 30%  $\text{K}_2\text{CO}_3$ , Other conditions as in Fig 3



### Effect of using a diaphragm (Fig.5)

The importance of the use of a diaphragm for better current efficiency is clearly seen but the difference is greater at lower concentrations of percarbonate probably due to competing cathodic reduction and auto-decomposition of percarbonate. The rate of auto-decomposition is bound to be higher at the higher percarbonate concentrations, thus reducing the effect of diaphragm.

Fig.5 Effect of diaphragm on potassium percarbonate formation  
Sodium silicate : 4 g/l; Other conditions same as in fig.4.



### Longer duration electrolysis

Result of continuous electrolysis is shown in Fig.6 for  $\text{Na}_2\text{C}_2\text{O}_6$  and in Fig.7 for  $\text{K}_2\text{C}_2\text{O}_6$ . The decreasing current efficiency curves show unstable nature of the percarbonate in spite of the addition agents. It is seen that the current efficiency gradually decreases during electrolysis. This is due to the higher rate of auto-decomposition of percarbonate with increase of its concentration in spite of the presence of the stabiliser.

Fig.6: Long duration experiment for sodium percarbonate

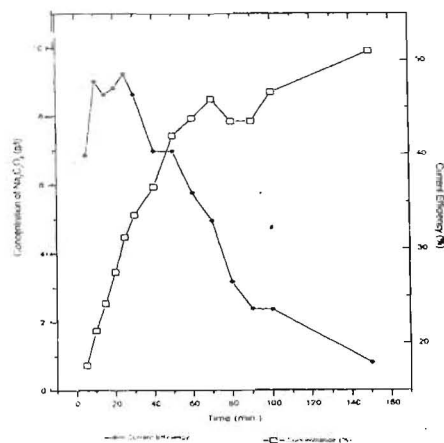
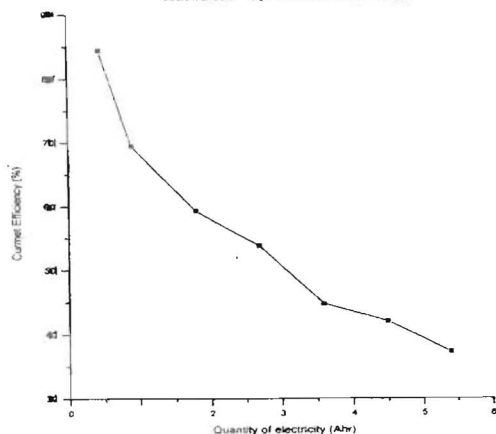


Fig.7: Longer duration experiment for potassium percarbonate formation

Sodium silicate : 2 g/l. Other conditions as in Fig.4



### CONCLUSION

The effect of several parameters viz. anode and cathode current density, temperature, electrolyte and addition agent composition and duration of electrolysis on the C.E for sodium and potassium percarbonate formation has been studied. Optimum conditions have been determined – Anode current density  $20 \text{ A/dm}^2$ , cathode current density  $2.5 \text{ A/dm}^2$  (due to the lower voltage), temperature  $283\text{K}$ , addition agent – sodium metasilicate  $4 \text{ g/l}$  for the sodium percarbonate and anode current density of  $40 \text{ A/dm}^2$ , potassium carbonate of  $300 \text{ g/l}$ , temperature of  $-263\text{K}$  and sodium silicate  $2 \text{ g/l}$  are for the potassium salt.

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