ELECTROLYTIC PREPARATION OF SODIUM AND POTASSIUM PERCARBONATE

G. Manoharan* M. Muthu Mohamed**, N. S. Raghavendran and K. C. Narasimham

Central Electrochemical Research Institute, Karaikudi 630 006

* Khadir Mohideen College, Adirampattinam 614 701
** Jamal Mohamed College, Tiruchirappalli

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 Na$_2$C$_2$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 $\times$ 2.2 cm $\times$ 0.1 mm) and (5.2 cm $\times$ 4.8 cm) were kept centrally, for the sodium and potassium percarbonate respectively - flanked by two perforated stainless steel cathodes (7.1 cm $\times$ 6.1 cm) wrapped with terylene diaphram. 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 H$_2$SO$_4$ was added to 5 ml of the solution, and this solution was titrated against standard 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/dm² for sodium percarbonate formation. Similarly for potassium percarbonate medium current density of 40 - 60 A/dm² 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.

Variation of temperature

Table II for Na₂C₂O₆ and Fig.2 for K₂C₂O₆ 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 K₂C₂O₆ formation, but the range of temperature studied is not known.

Table I

<table>
<thead>
<tr>
<th>Composition of Electrolyte</th>
<th>Saturated solution of sodium carbonate (120 g/l)</th>
<th>Sodium metasilicate 3g/l</th>
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<tbody>
<tr>
<td>Temperature</td>
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</tbody>
</table>

<table>
<thead>
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<th>S.No.</th>
<th>Anode Current density (A/dm²)</th>
<th>Cathode Current density (A/dm²)</th>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>Current efficiency (%)</th>
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</thead>
<tbody>
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<td>4.6</td>
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<tr>
<td>2</td>
<td>20</td>
<td>5.0</td>
<td>4.9</td>
<td>2</td>
<td>38.5</td>
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<tr>
<td>3</td>
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<td>10.0</td>
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</table>

Table II

<table>
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<tr>
<th>Electrolyte</th>
<th>Saturated solution of Na₂CO₃ Na₂SiO₃ : 3g/l</th>
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</thead>
<tbody>
<tr>
<td>Current density</td>
<td>20 A/dm² (anodic)</td>
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<tr>
<td>Current density</td>
<td>2.5A/dm² (cathodic)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S. No.</th>
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<th>Voltage (V)</th>
<th>Saturated solution (Na₂CO₃) g/l</th>
<th>5 min</th>
<th>15 min</th>
<th>30 min</th>
<th>Current efficiency (%)</th>
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<tr>
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<td>31.6</td>
<td>12.4</td>
<td>17.3</td>
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</tr>
</tbody>
</table>
Electrolytic Preparation of Sodium and Potassium Percarbonate

Variation of cathode current density

Only a slight difference in current efficiency was seen for the two cathode current densities studied (8 A/dm² and 2.5 A/dm²) (for Na₂C₃O₆) 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 A/dm² and should not be less than 10 A/dm² [14].

Variation of concentration (Fig.3)

For Na₂C₃O₆, a saturated solution of Na₂CO₃ (120 g/l) has been used as electrolyte. An initial electrolyte concentration of 10 – 30% is seen to be optimum for K₂C₃O₆. Higher concentrations result in lower current efficiencies.

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 Na₂C₃O₆. For K₂C₃O₆, 2 g/l Na₂SiO₃ 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 K₂SiO₃ concentration (0.15-1.5 g/l) in 4M K₂CO₃ current efficiency for K₂C₃O₆ synthesis increases and rate constant of its thermal decomposition decreases.

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.

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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 Na$_2$CO$_3$ and in Fig.7 for K$_2$CO$_3$. The decreasing current efficiency curves show unstable nature of the percarbonate inspite 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.

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 A/dm$^2$, cathode current density 2.5 A/dm$^2$ (due to the lower voltage), temperature 283k, addition agent – sodium metasilicate 4 g/l for the sodium percarbonate and anode current density of 40 A/dm$^2$, potassium carbonate of 300 g/l, temperature of -263k and sodium silicate 2 g/l are for the potassium salt.

References
1. Risenfeld and Reinhold, Ber. 42 (1909) 4377.
2. Salzer, ibid., 8 (1902) 900.