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An electrochemical device for oxygen production avoiding the generation of hydrogen

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An electrochemical device for oxygen production which makes oxygen on both cathode and anode from air has been developed. The electrolytic cell consists of an air cathode, a catalytic decomposition mesh and a nickel anode. The electrolyser is composed of six single cells. The working surface area of a single cell is $0.02\,m^2$. Performance depends on factors such as the basic electrolyte concentration, temperature, air flow rate, gas flow distribution and current density. When the device is operated with 7 M KOH at room temperature and with an air flow rate of $0.4\,m^3\,h^{-1}$ and current of 20 A, the oxygen evolution rate is $0.036\,m^3\,h^{-1}$ and the oxygen purity is 99.5%. The current efficiency is 72.0%. The device has operated continuously for 12 months with stable performance.

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1. Introduction

In the past, most medical oxygen has been provided from oxygen cylinders. Because of the inconvenience of cylinder transport and refilling, it is very difficult for undeveloped regions to use oxygen where transport is limited. Furthermore, besides the low purity of cylinder oxygen, users are often concerned about high-pressure operation. For these reasons, Wynveen, Tseung and Furuya *et al.* [1–3] proposed the production of oxygen using air cathodes [4–7]. The present programme of work has studied this oxygen-producing method for more than three years [8–10]; prototypes have been made and are under test in hospitals. These have proved very effective. Some aspects of the performance of such devices are discussed in this paper.

2. Fundamental principles of oxygen production

An air cathode takes the place of the hydrogen-evolution electrode in water electrolysis and a catalytic decomposition mesh is mounted between the cathode and anode. When power is on, atmospheric oxygen is initially reduced to hydrogen peroxide ions on the air cathode, and is then decomposed to oxygen and hydroxyl ions after contact with the catalytic decomposition mesh. At the same time, the hydroxyl ions formed are oxidized to oxygen and water on a nickel anode (see Fig. 1). Thus, duet oxygen production is achieved. The electrochemical and catalytic decomposition reactions are as follows:

cathode reaction

$$O_2(\text{air}) + H_2O + 2e^- \longrightarrow HO_2^- + OH^- \qquad (1)$$

decomposition reaction

$$HO_2^- \xrightarrow{\text{cat.}} \frac{1}{2}O_2 \uparrow + OH^- \qquad (2)$$

anodic reaction

$$2OH^- \longrightarrow \frac{1}{2}O_2 \uparrow + H_2O + 2e^- \qquad (3)$$

It can be seen from Equations 1–3 and Fig. 1 that electrochemical duet oxygen production is achieved on the basis of the principle of the combinations of the cathodic and anodic reactions and the catalytic decomposition reaction.

This method is a two-electron reaction and its theoretical decomposition voltage is +0.48 V, while oxygen production by water electrolysis is a four-electron reaction and its theoretical decomposition voltage is +1.23 V. Therefore, when this method is compared with water electrolysis, not only does the theoretical decomposition voltage decrease by 0.75 V, which leads to a decrease in energy consumption, but the amount of oxygen evolved is doubled for the same charge passed. Because oxygen is generated selectively on both cathode and anode, while no hydrogen is formed, it is not necessary to have a diaphragm in the cell and the purity of oxygen is very high. In addition, oxygen in the air and electric energy are consumed to produce oxygen, while no water in the electrolyte solution is consumed. Thus the system is convenient to use and maintain.

3. Experimental details

3.1. *Composition and preparation of electrodes*

3.1.1. Preparation of water-proof gas-diffusion oxygen cathode. The water-proof gas-diffusion oxygen cathode (air cathode) is mainly composed of a water-proof conductive permeable film, conductive mesh and catalytic membrane. The structure is shown in Fig. 2. The preparation methods of the water-proof conductive permeable film and conductive mesh are the same as those described in

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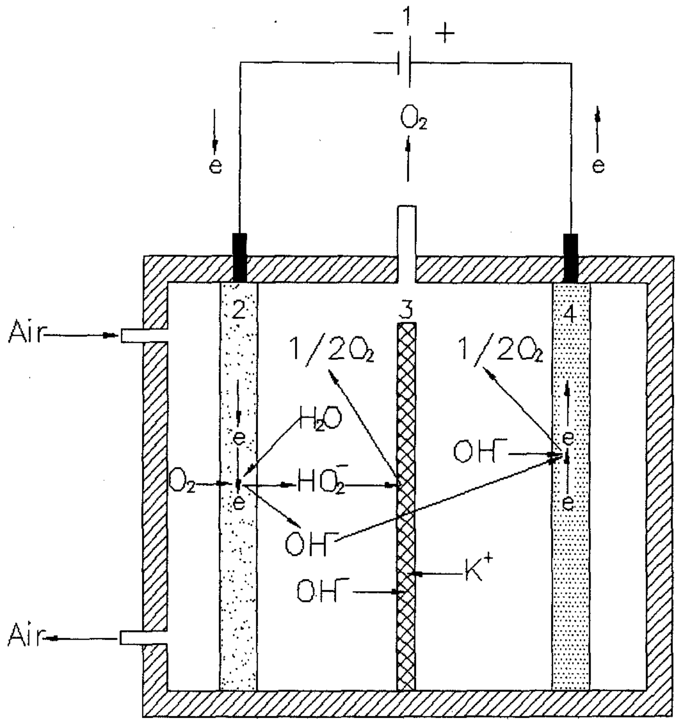

Fig. 1. Principle of electrochemical oxygen production avoiding the generation of hydrogen. Key: (1) d.c. power source; (2) air cathode; (3) catalytic decomposition mesh; (4) nickel anode.

the literature [7]. The catalytic membrane is made by mixing graphite powders prepared by vacuum grinding in a vibrating ball mill and 60% PTFE emulsion in a weight ratio of 10:3. After pressing the mixture at 50 °C, the cellulosic membrane is produced. The graphite powder content in the membrane is 20 mg cm^{-2}; the specific surface area of the graphite powder in the membrane is not less than 300 m^2 g^{-1}.

The catalytic membrane, conducting mesh and water-proof conductive permeable film are assembled according to Fig. 2. After cold pressing at 500 kg cm^{-2} and then sintering in air at 300 °C for 30 min, the air cathode is produced.

3.1.2. Preparation of catalytic decomposition mesh. 100 mesh stainless steel screen is used as support for the catalytic decomposition H_2O_2. The active material is 450 kg m^{-3} $Mn(NO_3)_2 \cdot 6H_2O$ solution. The active material is painted on to the support, followed by heat treatment at 180 °C for 1 h. The previous steps are then repeated five times. During the last stage of thermal decomposition, the stainless steel screen is heated to 360 ~ 380 °C, and the temperature is maintained for 2 h.

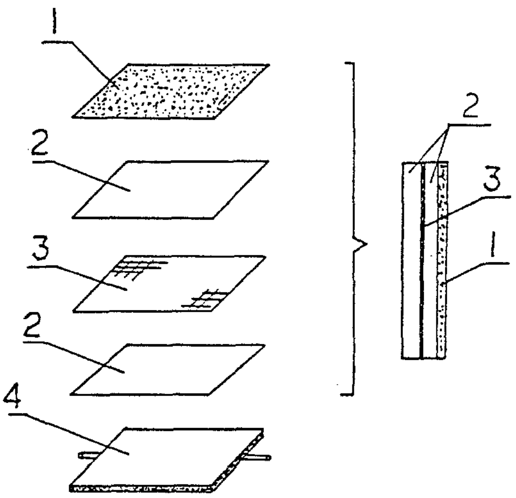

Fig. 2. Schematic illustration of the structure of the air cathode: (1) catalytic film; (2) water-proof conductive permeable film; (3) conductive mesh; (4) air chamber.

3.2. *Basic structure of the electrolytic cell*

The oxygen cathode is a water-proof gas-diffusion graphite catalytic electrode with a surface area of 0.01 m^2 and a nickel mesh is used as the anode. A manganese dioxide catalytic decomposition mesh is installed between the cathode and anode on which the hydrogen peroxide formed on the cathode is decomposed. The structure of a single cell is shown in Fig. 3. The practical combined cell is composed of six single cells and the working area of a single cell is 0.02 m^2. The designed electrolysis current is 20 A and the oxygen output is 0.03 m^3 h^{-1}.

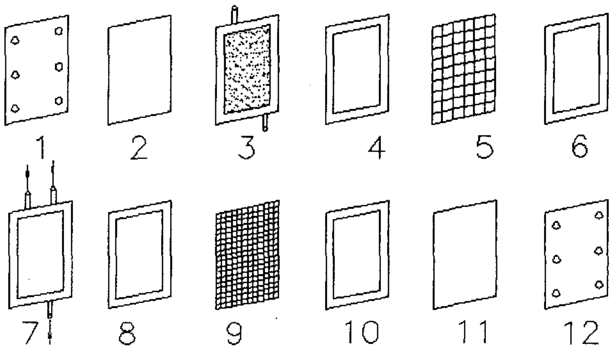

Fig. 3. Diagrammatic sketch of a single cell: (1,12) end plate; (2,11) pad; (3) oxygen cathode; (4,6,8,10) grommet; (5) catalytic decomposition mesh; (7) electrolyte chamber; (9) anode.

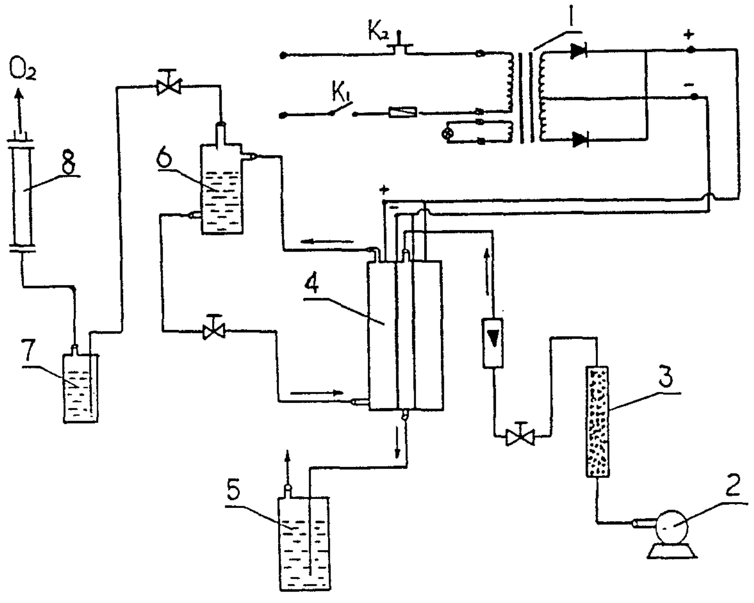

Fig. 4. Diagrammatic sketch of the oxygen producing process: (1) rectifier power source; (2) air pump; (3) soda lime column; (4) electrolytic cell; (5) tail gas bottle; (6) gas–liquid separator; (7) gas washing bottle; (8) desiccator.

3.3. *Oxygen production process*

The process is shown in Fig. 4. The working electrolyte is 7 M KOH aqueous solution and the working gas fed to the oxygen cathode is air.

During electrolysis, air is pumped through a soda lime drying column to remove impurities such as dust and carbon dioxide. Purified air is passed into the air chamber of the electrolytic cell. Residual gas passes to atmosphere through a tail gas bottle. The electrolyte flows into the electrolytic cell from a gas–liquid separator. Oxygen generated in the cell, together with the basic electrolyte, flows into the gas–liquid separator. Following separation the oxygen is purified in a gas washing bottle and a desiccator in series to give pure oxygen, while the electrolyte is recycled.

3.4. *Oxygen analysis*

Oxygen analysis was conducted according to the GB8986–88 (Method of the Medical and Aeronautical Oxygen Detection) in China.

4. Results and discussion

4.1. *Effects of gas distribution*

Compared with the single cell and the double cell [7,8], the air distribution of the combined cell is much more complicated. Figs 5 and 6 show the results of the series and parallel connections of air in the combined cell, respectively. It can be seen that when the gas flow is in series, the cell voltages of the single cell 1 and 2 are very low, while those of 3, 4, 5, 6 are very high. When the gas is in parallel connection, the cell voltages of the single cell 1 and 2 are very high, while those of 3, 4, 5, 6 are very low. The cell voltage distributions for series and parallel connection are in contrast, but the total effects of series connection are inferior to those of parallel connection. Later the parallel connection of gas flow was improved in order to attain uniform distribution of cell voltage among each single cell (curve (b), Fig 5) and to meet the demand of the electrolysis process.

4.2. *Effects of air flow rate*

Because air is used as reactant, its flow rate has a direct effect on the working characteristics of the reaction. Figures 7 and 8 show the relation between the air flow rate of a single cell and the cell voltage. It can be seen that, under low air flow rate, the cell voltage is high and the cell voltage distribution among each single cell is nonuniform, which illustrates that low air flow rate results in high polarization, poor cell working characteristics and insufficient air for the reaction. However, when the air flow rate increases, the cell voltage gradually falls and the cell voltage distribution among the single cells tends to be uniform, which

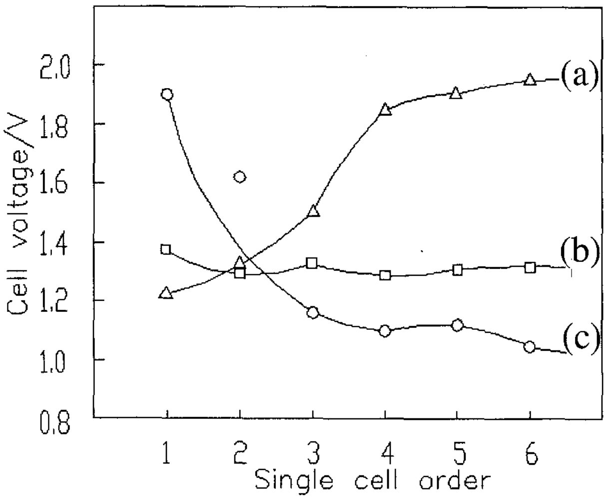

Fig. 5. Effects of air distribution method in the combined cell on the cell voltage. Curves: (a) series connection; (b) improved parallel connection; (c) parallel connection. Current: 20 A; room temperature.

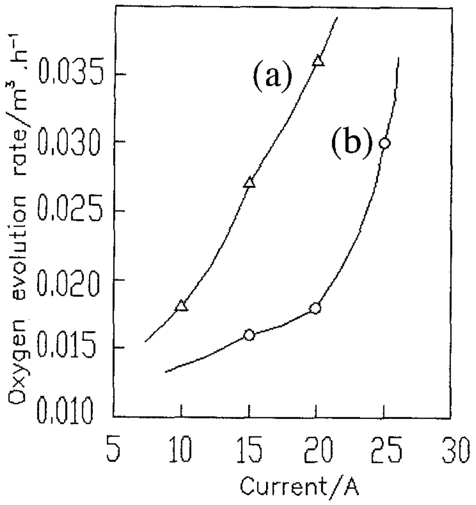

Fig. 6. Relations between current and oxygen evolution rate under different air distribution methods. Curves: (a) parallel connection; (b) series connection.

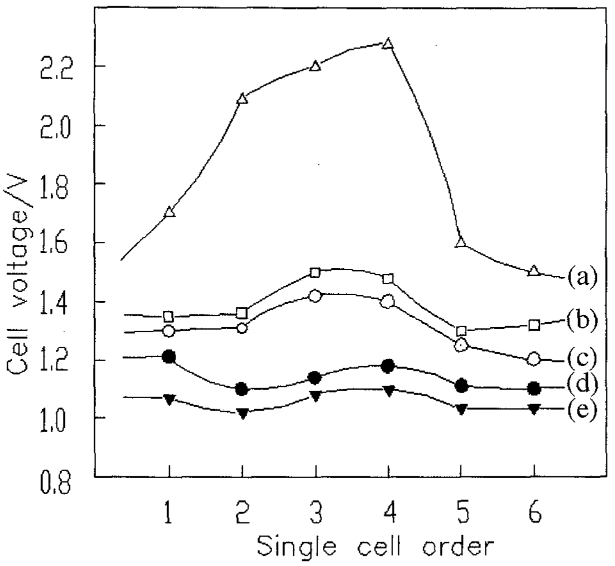

Fig. 7. Relation between air flow rate and cell voltage. Curves: (a) $0.12 m^3 h^{-1}$; (b) $0.28 m^3 h^{-1}$; (c) $0.36 m^3 h^{-1}$; (d) $0.52 m^3 h^{-1}$; (e) $0.76 m^3 h^{-1}$. Current: 15 A; room temperature.

illustrates that increase in the air flow rate leads to a remarkable decrease in cell voltage. However, it can be seen from curves (d) and (e) of Fig. 7 that when the air flow rate exceeds about $0.52 m^3 h^{-1}$, the rate of cell voltage reduction with respect to the rate of cell voltage reduction of low air flow rate is slow. Thus when the air flow rate is greater than that value, the cell voltage decreases insignificantly. The experiments indicate that when the air flow rate reaches $0.4 m^3 h^{-1}$, there is sufficient air for normal operation of the combined cell.

4.3. *Effects of current*

Figure 9 shows the relations between the current of the combined cell and the oxygen evolution rate, and the total cell voltage. It can be seen that for currents less than 20 A, the relation between the oxygen evolution rate and current is linear and the total cell voltage is 8.5 V. If the current is in excess of 25 A, the change in the oxygen evolution rate is slow, but the cell voltage curve increases linearly, which shows that when the polarization increases, the oxygen evolution rate decreases and the current efficiency falls. Thus, the current of the combined cell should be below 20 A.

4.4. *Effects of temperature*

The effects of temperature for the combined cell are shown in Fig. 10. It can be seen that, under the same current and electrolyte concentration conditions, the maximum oxygen evolution rate is obtained when the temperature is in the range 25 ~ 35 °C. The current efficiency is highest in this temperature interval. This result agrees with that for the single and double cell [7, 8]. Therefore, when the device is used to make oxygen, the temperature should be in the range 25 ~ 35 °C.

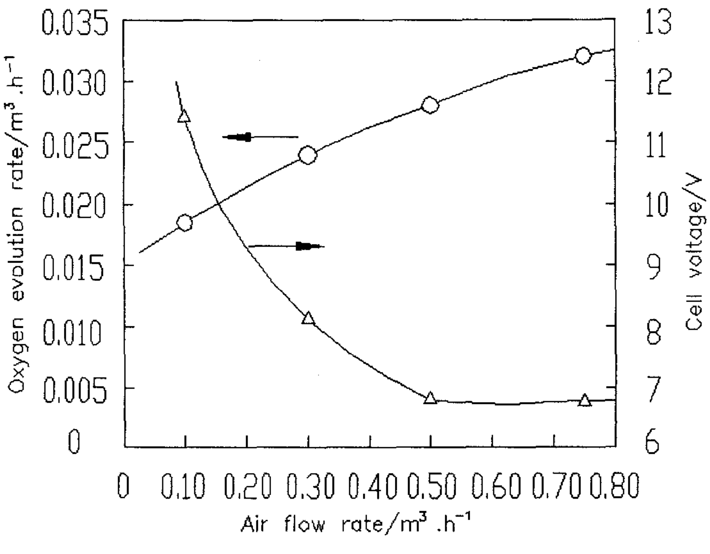

Fig. 8. Relations between the air flow rate and the oxygen evolution rate, and the total cell voltage. Current: 15 A; room temperature.

Table 1. Main results of the combined cell test

Current /A	*Current density* /A m^{-2}	*Total cell voltage* /V	*Theoretical oxygen evolution rate* /m^3 h^{-1}	*Actual oxygen evolution rate* /m^3 h^{-1}	*Current efficiency* /%	*Electrolysis energy consumption* /m^3 (kWh)$^{-1}$	*Oxygen purity* /%
10	500	5.64	0.025	0.019	76.0	0.336	99.8
15	750	6.86	0.0375	0.028	74.8	0.272	99.6
20	1000	8.30	0.050	0.036	72.0	0.216	99.4

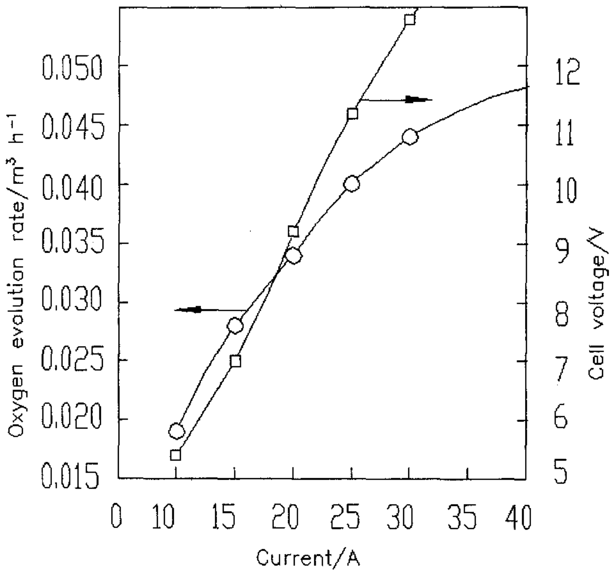

Fig. 9. Relations between current and oxygen evolution rate, and cell voltage. Air flow rate: 0.45 m^3 h^{-1}; room temperature.

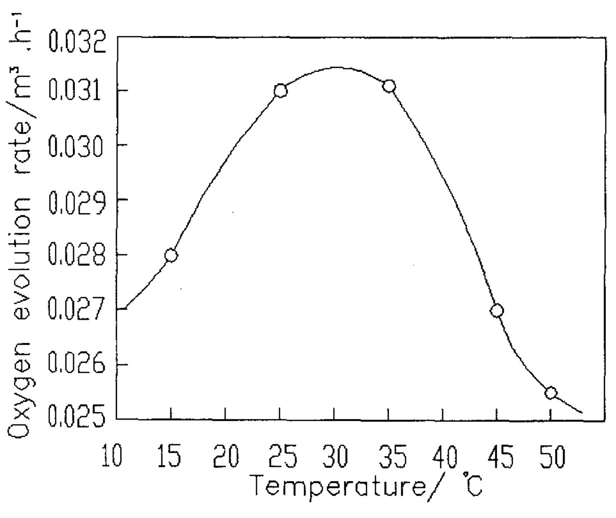

Fig. 10. Relation between temperature and oxygen evolution rate. Operating current: 18 A; air flow rate: 0.45 m^3 h^{-1}.

4.5. *Main results of the combined cell test*

The combined cell is composed of six single cells; the working area of a single cell is 0.02 m^2. Gas flow and the liquid flow are in parallel connection while the electric circuit is in series. The initial operating temperature is room temperature; air flow rate is 0.4 m^3 h^{-1}. The main test results are listed in Table 1. The data are almost identical to the single cell and double cell results [7, 8], which shows that the scale up effects of the system are small.

A prototype of the combined cell has been made. After continuous operation for 12 months, the device is still maintaining stable performance. The device is under test in several hospitals in Zhejiang province, China, with satisfactory results.

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