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An electrochemical oxygen separator using an ion-exchange membrane as the electrolyte

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An electrochemical oxygen separator based on oxygen reduction at an air cathode and oxygen evolution at an anode has been developed. The device features use of an ion-exchange membrane (Nafion 117) as the sole electrolyte and an air cathode mainly made of carbon.

The anode was formed by chemically plating platinum ($3.7\,\mathrm{mg\,cm^{-2}}$) on one side of the Nafion 117 membrane. The air cathode was bonded to the other side of the membrane by spraying a slurry of graphitized furnace black loaded with platinum, followed by hot-pressing. The addition of a Nafion solution and a PTFE dispersion to the slurry was essential. The ultimate loading of platinum for the cathode was $0.2\,\mathrm{mg\,cm^{-2}}$. An electrochemical oxygen separator with a working area of $100\,\mathrm{cm^2}$ was constructed. When the separator was used as an oxygen concentrator it could be operated at $200\,\mathrm{mA\,cm^{-2}}$ and produced $70.9\,\mathrm{cm^3\,min^{-1}}$ of oxygen with a purity of 98.4%. When the separator was used as a circulation-type oxygen removal system it reduced the oxygen concentration of a 10-$\mathrm{dm^3}$ chamber to less than 0.02% within 70 min. When the separator was used as a flow-through-type oxygen remover, air with an oxygen concentration of 0.02% was produced at $100\,\mathrm{cm^3\,min^{-1}}$.

1. Introduction

When air is supplied to the cathode of an electrochemical cell consisting of an air cathode, an oxygen-evolving anode and an electrolyte, and an external potential is applied between the electrodes, oxygen in the air is selectively reduced electrochemically at the cathode and is liberated at the anode. Such an electrochemical cell thus functions as a separator of oxygen from air. If it is intended to utilize the oxygen liberated at the anode the electrochemical oxygen separator can be regarded as an oxygen concentrator [1–3]. If it is intended to utilize oxygen-depleted air vented from the air cathode compartment it can be regarded as an oxygen remover [4, 5].

In the previously reported electrochemical oxygen separator [4], an aqueous solution of KOH or H_2SO_4 was used as the electrolyte. However, if aqueous electrolytes leak out or flow into the oxygen stream as mist the clean-up is very troublesome. The change in electrolyte concentration due to evaporation and absorption of water is another problem. In view of these factors, use of an ion-exchange membrane as the electrolyte, as proposed by Maget [6], is advantageous. However, there is little published work concerning electrochemical oxygen separators using ion-exchange membranes.

SPE fuel cell technology [7] relates strongly to the development of an electrochemical oxygen separator. Since the present application of SPE fuel cells is limited to space power sources where cost matters little, expensive noble metals have been used exclusively as electrode materials and cheaper carbon has not been used. Recently, we found that in making an air cathode embedded onto an ion-exchange membrane electrolyte (Nafion), the addition of a Nafion solution to the air cathode, mainly made of carbon loaded with platinum catalyst, resulted in a remarkable improvement of the characteristics of the air cathode due to an increase in active sites [8]. This paper describes an electrochemical oxygen separator using an ion-exchange membrane electrolyte based on the above finding.

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2. Fabrication of the electrochemical oxygen separator

2.1. *Bonding of electrodes onto the ion-exchange membrane*

As the ion-exchange membrane, a Nafion 117 membrane (0.18 mm thick; ion-exchange capacity, 0.91 meq g^{-1}) manufactured by Du Pont, was used. This membrane was treated with acetone, immersed in boiling water for 30 min, treated with 1.2 M HCl and then rinsed with ion-exchanged water. The platinum anode was plated onto one side of the pretreated Nafion 117 membrane in the following manner [9] which is a partial improvement of the electroless plating method proposed by Torikai and Takenaka [10]. First, H^+ within the Nafion 117 membrane was replaced by $(Pt(NH_3)_5Cl)^{3+}$ by contacting the membrane with an aqueous solution of $(Pt(NH_3)_5Cl)Cl_3$ (platinum 2 mg cm^{-3}). Then, $(Pt(NH_3)_5Cl)^{3+}$ was reduced by a 0.04% $NaBH_4$ solution placed on one side of the membrane and platinum nuclei (0.4 mg cm^{-2}) were formed on that surface of the membrane. An aqueous mixed solution (pH 0.3) of 0.35 mol dm^{-3} H_2PtCl_6 and 0.1 mol dm^{-3} N_2H_4 2HCl was then applied to the membrane and platinum deposits were grown on the platinum nuclei. The final quantity of deposited platinum was 3.7 mg cm^{-2}. The air cathode was bonded onto the other side of the membrane in the following manner [8]. A slurry mixture of graphitized furnace black powder loaded with 10% platinum (1.3 g), water (19 cm^3), isopropanol (29 cm^3), a 5% Nafion 117 solution in a mixture of a lower aliphatic alcohol and water (Aldrich Chemical Company) (11.1 cm^3) and a 60% PTFE dispersion (2.1 cm^3) was sprayed onto the Nafion 117 membrane, followed by hot-pressing at 100° C and 175 kg cm^{-2}. The loaded amount of platinum was 0.2 mg cm^{-2}.

The reason why different methods were used for fabrication of the anode and cathode is as follows. The electroless plating method was adopted for bonding the anode onto the membrane since the platinum catalyst anode bonded onto the membrane by the electroless plating method is more hydrophilic than that bonded by the hot-pressing method and water can penetrate into the membrane much more easily. The hot-pressing method with PTFE as the binder was adopted to bond the air cathode onto the membrane since in the air cathode the contact areas between hydrophilic sites and hydrophobic sites become reaction sites and thus PTFE is essential.

2.2. *Construction of the electrochemical oxygen separator*

Behind the cathode and anode sides of the Nafion 117 membrane–electrodes composite, current collectors made of expanded titanium plated with platinum, terminal plates made of titanium, an air feed plate or a water feed plate made of polypropylene and end-plates made of stainless steel were arranged in that order and all the elements were secured by tie rods. Electrochemical oxygen separators with working areas of 10 cm^2 (ϕ 36 mm) and 100 cm^2 (100 × 100 mm) were fabricated. The construction of the 10 cm^2 cell is shown in Fig. 1. In this cell a Luggin capillary was attached to the periphery of the Nafion 117 membrane (portion without electrodes) to enable measurement of the air cathode potential versus SCE. The construction of the 100 cm^2 cell is shown in Fig. 2.

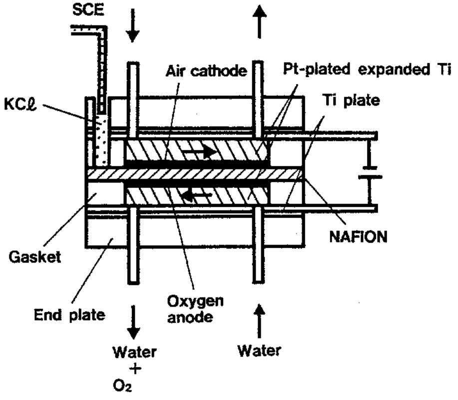

Fig. 1. Cross-sectional view of the electrochemical oxygen separator (10 cm^2).

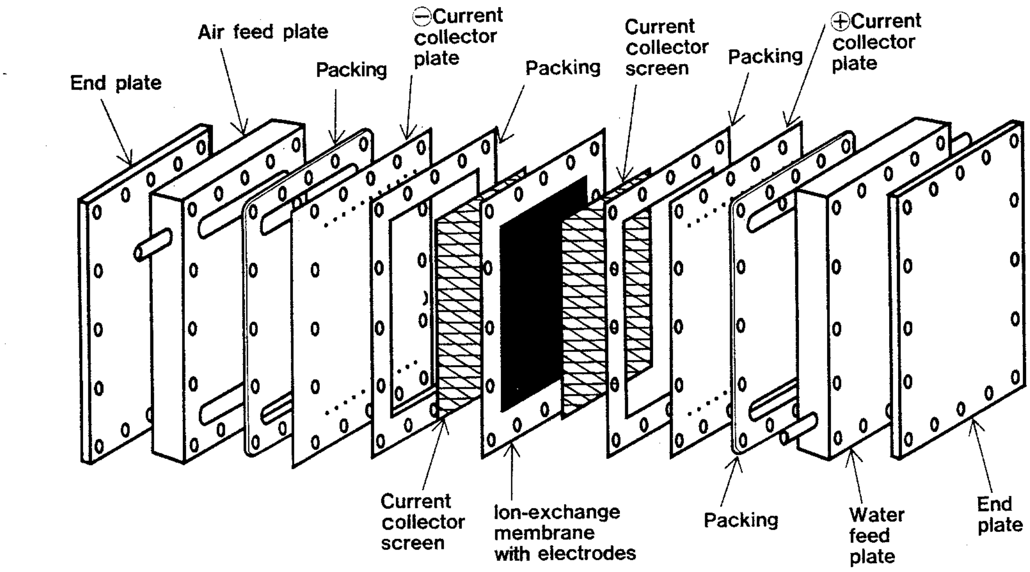

Fig. 2. Exploded view of the electrochemical oxygen separator (100 cm^2).

3. Experimental details and discussion

3.1. *I–V characteristics and hydrogen evolution voltage of the electrochemical oxygen separator*

Fig. 3 shows the *I–V* characteristics of the electrochemical oxygen separator with a working area of 10 cm^2 when water at 40° C with specific resistance of 5 MΩ cm was circulated via the anode cavity of the electrochemical oxygen separator and air at room temperature was supplied to the cathode at a feed rate of 4 dm^3 min^{-1}.

There are two reasons why the water temperature is maintained at 40° C. First, 40° C is the lowest temperature which can be easily maintained constant when the room temperature changes and secondly, the temperature in the chamber of an incubator is usually maintained at 37–40° C.

In the electrochemical oxygen separator the following reactions normally occur.

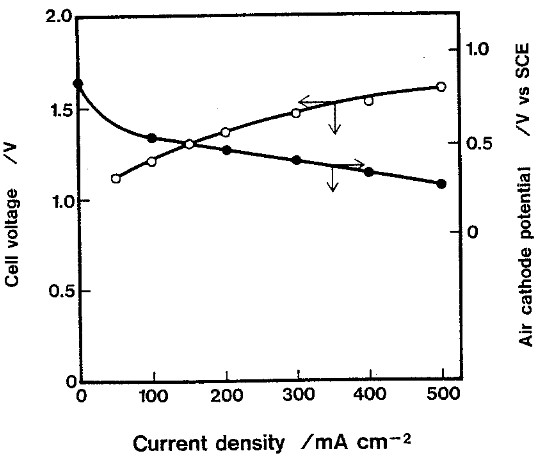

Fig. 3. Polarization characteristics of the electrochemical oxygen separator. Air cathode area, 10 cm^2; water temperature, 40° C; air feed rate, 4 dm^3 min^{-1}.

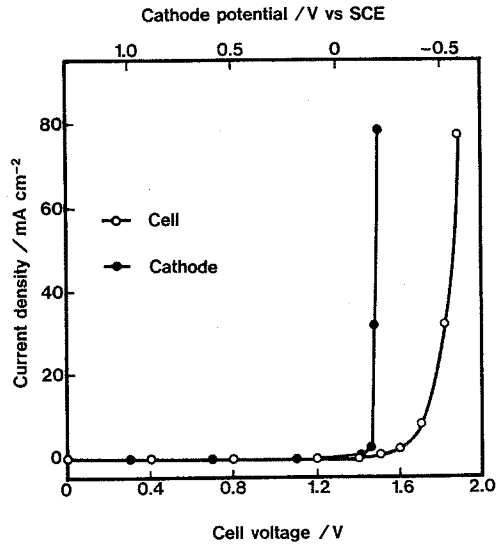

Fig. 4. *I–V* characteristics of the electrochemical oxygen separator without air feed. Cathode area, 10 cm^2; water temperature, 40° C.

At the cathode: $\frac{1}{2}O_2 + 2H^+ + 2e \rightarrow H_2O$ (1)

At the anode: $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e$ (2)

However, when the air cathode deteriorates or the oxygen concentration in the atmosphere in contact with the air cathode is reduced through removal of oxygen, the following reaction may occur in place of the cathode reaction 1:

$$2H^+ + 2e \rightarrow H_2 \qquad (3)$$

The *I–V* characteristics of the electrochemical oxygen separator without air feed are shown in Fig. 4. Hydrogen evolves in the region where the terminal voltage is higher than 1.4 V and the cathode potential is more negative than − 0.16 V versus SCE at 40° C. The highest current density at which the electrochemical oxygen separator is able to eliminate the possibility of hydrogen evolution is ~200 mA cm^{-2} from Fig. 3.

3.2. *Oxygen generation and oxygen removal characteristics of the electrochemical oxygen separator*

The electrochemical oxygen separator with a working area of 100 cm^2 was operated under the following conditions: water at 40° C was circulated via the anode cavity, air at 25° C was supplied to the cathode at a feed rate of 4 dm^3 min^{-1} and a current of 20 A (200 mA cm^{-2}) was passed through the electrochemical cell. The rate of oxygen generation at the anode was measured by means of a soap membrane-type precision flowmeter. The oxygen generation rate was 70.9 cm^3 min^{-1} at 101.3 kPa and 25° C. The concentration of oxygen vented from the anode compartment was 98.4%. The oxygen separation efficiency (current efficiency) with the oxygen purity taken into account was 91.3%.

Takenaka *et al.* [11] have reported that the current efficiency of their water electrolysis cell using an electrodes–Nafion membrane composite in which catalyst electrodes were bonded to a Nafion membrane by an electroless plating method was 95–96% and the purity of oxygen evolved from the anode was 99.94–99.98%. The rather higher purity of oxygen, in spite of the low current efficiency, is attributable to back-diffusion of hydrogen evolved at the cathode and recombination of hydrogen with oxygen at the anode. In the case of the electrochemical oxygen separator, the purity of oxygen should be much lower than in the case of the water electrolysis cell, since nitrogen in the air cathode cavity will diffuse to the anode through the Nafion membrane and nitrogen is not consumed as is hydrogen.

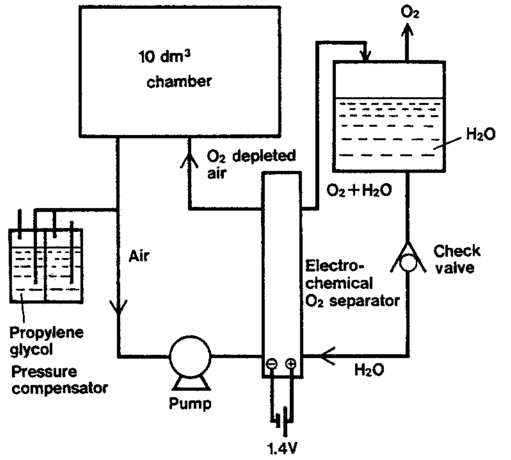

Fig. 5. Schematic diagram of the circulation type oxygen removal system.

The electrochemical oxygen remover may be used in two modes, i.e. the circulation mode and flow-through mode. Characteristics of the circulation mode were studied in the following manner. As depicted in Fig. 5, the cathode cavity of the electrochemical oxygen separator (100 cm^2) was linked to a chamber with an internal volume of 10 dm^3 via an air circulation pump and a pressure compensator with a liquid valve filled with propyleneglycol. Air in the circulation loop was circulated at the rate of 4 dm^3 min^{-1} and a constant potential of 1.4 V was applied to the electrochemical oxygen separator. As shown in Fig. 6 the oxygen concentration in the chamber and the current decreased gradually with time and the oxygen concentration reached 0.02% in 70 min. The oxygen removal capability of the electrochemical oxygen separator may be represented by the mean current density averaged over the oxygen removal period. The mean current density calculated from Fig. 6 was 109 mA cm^{-2}. In the case of the electrochemical oxygen separator with KOH or H_2SO_4 as the electrolyte, the mean current density at the safe applied potential without hydrogen evolution

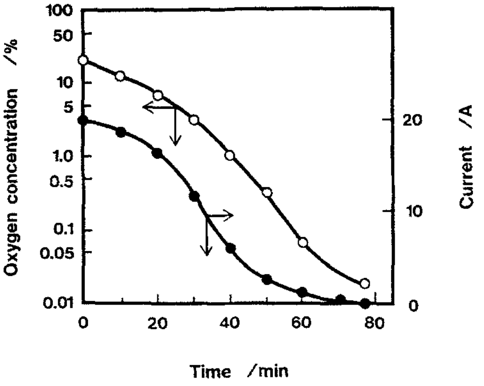

Fig. 6. Oxygen removal characteristics of the circulation type oxygen removal system. Internal volume of chamber, 10 dm^3; air cathode area, 100 cm^2; water temperature, 40° C.

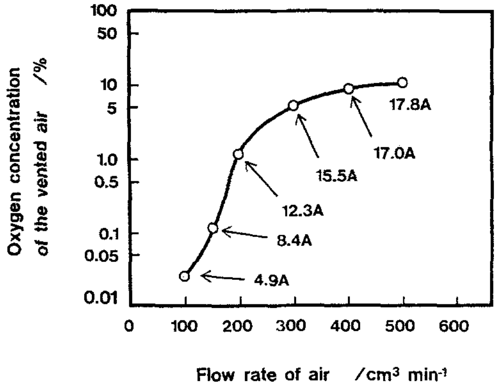

Fig. 8. Oxygen removal characteristics of the flow-through type oxygen removal system. Air cathode area, 100 cm^2; water temperature, 40° C.

was 32 mA cm^{-2} or 24 mA cm^{-2}, as previously reported [4]. Therefore, the electrochemical oxygen separator with the ion-exchange membrane electrolyte has a superior oxygen removal capability to separators using liquid electrolytes. Electrochemical oxygen separators with ion-exchange membrane electrolytes should be more expensive than those with liquid electrolytes when compared at the same working area, but not necessarily when compared at the same oxygen removal capability.

The oxygen removal characteristics in the flow-through mode were studied in the following manner. As depicted in Fig. 7, air was supplied to the inlet of the cathode cavity and a constant potential of 1.4 V was applied to the electrochemical oxygen separator. The relationship between the feed rate of air and the oxygen concentration of the oxygen-depleted gas vented from the cathode cavity was determined. The oxygen removal characteristics in the flow-through mode are shown in Fig. 8. The decrease in the air feed rate was accompanied by a decrease in oxygen concentration of air from the outlet of the air cathode cavity. When the air feed rate was 100 cm^3 min^{-1}, a gas stream mainly of nitrogen with an oxygen concentration as low as 0.02% was produced.

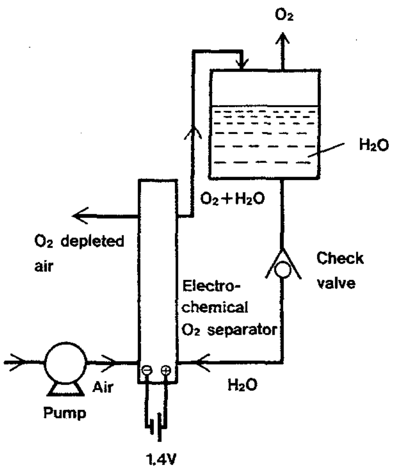

Fig. 7. Schematic diagram of the flow-through type oxygen removal system.

3.3. *Life tests of electrochemical oxygen separators*

Atmospheric air was supplied to the air cathode of the electrochemical oxygen separator with a working area of 100 cm^2. Intermittent operations of 7.5 h per day at 200 mA cm^{-2} were repeated and the cell voltage was measured daily. Comparison of two water feed modes was made. In the first mode, water was circulated via the anode cavity at a constant temperature of 40° C and water vented from the cathode cavity was discarded. In the second mode, water vented from the cathode cavity was returned to the water tank and recirculated to the anode cavity. The effect of two air humidity levels was studied. In the first case air was fed at an ambient humidity and in the other case air was humidified at 40° C. The results of life tests are summarized in Fig. 9. Under all operational conditions the voltages of the electrochemical oxygen separator remained almost constant

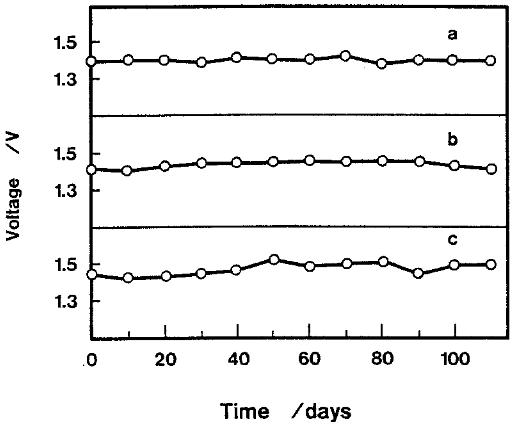

Fig. 9. Life tests of electrochemical oxygen separators. Air cathode area, 100 cm^2; water temperature, 40° C; air feed rate, 4 dm^3 min^{-1}; operation current, 20 A; operation mode, intermittent (7.5 h per day). (a) Water generated at the air cathode was discarded. (b) Water generated at the air cathode was recirculated to the anode. (c) Air was humidified.

throughout the operation period which exceeded 100 days.

Operation of the oxygen separator is accompanied by the transfer of water from the anode to the cathode due to the electrode reactions, 1 and 2, and electro-osmosis [12]. The theoretical rate of water transfer is estimated to be as much as 53.5 g h^{-1} when the electrochemical oxygen separator is operated at 20 A (200 mA cm^{-2}) [8].

Therefore, if the water transferred from the anode to the cathode is discarded, too much water in the water tank would be needed. For the effective utilization of water it is better that the water collected in the cathode cavity is recirculated to the water tank. However, the recirculation of water might lead to accumulation by the membrane of cationic impurities from electrodes, current collectors and packing materials, thus affecting the electric conductivity of the membrane. The results in Fig. 9b showed that this problem did not occur.

Recently, demand for the addition of oxygen concentration control functions to incubators for cultivating cellular tissue and bacteria has increased. Oxygen concentration is usually controlled by use of oxygen and nitrogen cylinders. The electrochemical oxygen separator can replace these cylinders. In this potential application of the electrochemical oxygen separator the entire gas circulation loop is maintained at 37–40° C and the relative humidity of the gas is nearly 100%. This prompted a life test in which air was saturated with water at 40° C. There was concern that humidification of air might lead to flooding of the cathode with water and accelerate the deterioration of the air cathode. However, Fig. 9c indicates that humidification of the air affects neither the initial performance nor the life of the air cathode.

4. Conclusions

Electrochemical oxygen separators using ion-exchange membranes as the sole electrolyte and air cathodes made mainly of carbon were developed. The electrochemical oxygen separator has two functions, oxygen generation and oxygen removal. In the former mode, this device works as an on-site oxygen generator or can be used as an oxygen source of an on-site ozone generator. In the latter mode the device can be used for cultivation of anaerobic bacilli. When both the oxygen generation function and the oxygen removal function are utilized the device can serve as an oxygen concentration control system [13].

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