

An integrated electrochemical–chemical method for the extraction of O₂ from air

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Oxygen can be extracted from ambient air by using a platinum cathode to reduce oxygen and by simultaneously evolving oxygen on a platinum anode. This leads to lower power consumption than when electrolyzing water to produce oxygen. A novel, integrated electrochemical–chemical method is described in this paper. The system consists of a Teflon-bonded graphite cathode which reduces oxygen via a two-electron process with the formation of HO₂ intermediate. By placing a NiCo₂O₄-covered nickel screen in the anode compartment, HO₂ is chemically decomposed to yield O₂; a separate Teflon-bonded NiCo₂O₄ anode evolves O₂ electrolytically. At 40°C and in 5 M KOH, the power consumption of this device is only 2.69 kW h l⁻¹ of O₂, significantly lower than conventional electrochemical oxygen extractors (4.38 kW h l⁻¹ O₂).

1. Introduction

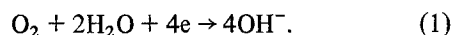
Portable oxygen generators are finding increasing applications in field hospitals, village clinics in developing countries, welding and high-altitude fighter aircraft. There are two basic types of oxygen generators: chemical generators, which use expensive chemicals, and electrochemical generators, which either electrolyze water or extract oxygen from the air by using an oxygen-reduction cathode coupled to an oxygen-evolution anode [1, 2].

This paper gives some preliminary results on an integrated electrochemical–chemical method which shows promise of significantly reducing the capital as well as the running costs of portable oxygen generators [3].

2. Oxygen generation by electrochemical methods

The most common method is to electrolyze water to produce H₂ and O₂. The theoretical voltage for electrolyzing water at 25°C is 1.23 V but the high overvoltage at the anode increases the operating voltage to about 2.2 V at 100 mA cm⁻². Moreover, the production of H₂ as the by-product, apart from increasing the power consumption, is a potential hazard in situations where portable oxy-

gen generators are used. A more efficient method is to use a Teflon (PTFE)-bonded, platinum black, fuel-cell cathode to reduce the oxygen in the ambient air to form OH⁻:



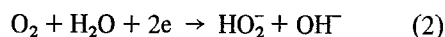
The OH⁻ diffuses through a suitable membrane, such as woven asbestos or glass-fibre mat, to an oxygen-evolving anode which liberates O₂. At 25°C, the potential of a Teflon-bonded, platinum black, air cathode in 5 M KOH at 100 mA cm⁻¹ is 0.8 V versus the reversible hydrogen electrode (RHE). The performance of a similar electrode when polarized anodically gives 100 mA cm⁻² at ~1.9 V versus RHE. Thus the working voltage of the cell, taking into account the unavoidable *iR* losses, will be 1.3–1.4 V, significantly lower than the 2.2 V (25°C) for electrolysis cells.

Though this type of oxygen extractor is an improvement over the traditional water electrolysis cell for the production of oxygen, its capital and running costs are still relatively high and use is limited to specialized applications.

3. An integrated electrochemical–chemical approach to the problem

Berl [4] showed that the reduction of oxygen on

graphite or carbon is a two-electron process which follows the perhydroxyl ion route:



This means that when such electrodes are used in a fuel cell, they are not as efficient as cathodes which directly reduce oxygen to hydroxyl ions via a four-electron process. Therefore, it is usual to add peroxide decomposition catalysts [5] to the carbon cathode, so that the HO_2^- produced can be decomposed, thus yielding O_2 for recycling, leading to higher efficiency [6]. On the other hand, if such electrodes were used in an oxygen extraction cell, the fact that the reduction of O_2 on carbon surfaces proceeds via a two-electron step could be beneficial, provided the HO_2^- was chemically decomposed and collected in the anode compartment. In this way, the number of coulombs required for the oxygen extraction process will be halved, leading to significant reduction in power consumption.

4. Experimental

4.1. Choice of materials

Earlier studies [7, 8] have shown that graphite powders with high surface areas ($500\text{--}600\text{ m}^2\text{ g}^{-1}$), prepared by vacuum grinding of graphite in a vibrating ball mill, possess very high activity for oxygen reduction in alkaline solution. This material was therefore chosen for this study. Johnson Matthey fuel-cell-grade platinum black ($30\text{ m}^2\text{ g}^{-1}$) was used as the cathode catalyst in some experiments. Two types of catalysts were evaluated as H_2O_2 decomposition catalysts: CoFe_2O_4 [5] and NiCo_2O_4 [9]. NiCo_2O_4 was exclusively used as the anode catalyst, since it has been shown to be more active than platinum black for the oxygen evolution reaction [10].

4.2. Preparation of electrodes

Two types of electrode were used:

(a) Screen electrodes, prepared by dipping 100-mesh nickel screens into 2 M Ni–Co nitrate solution (Ni:Co = 1:2) and then heating in air at 400°C for 10 hours. The formation of NiCo_2O_4 spinel on the electrode surface was confirmed by X-ray powder diffraction.

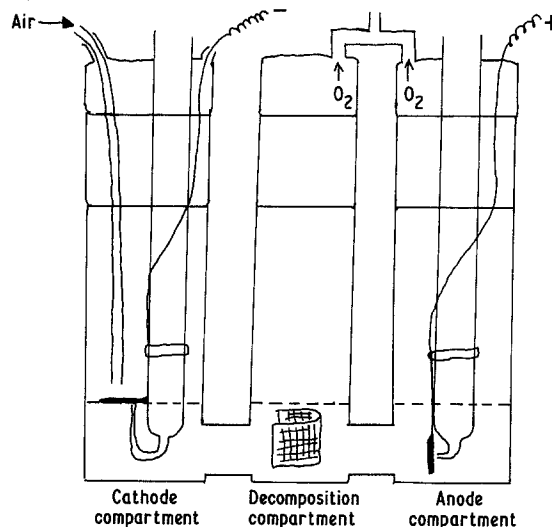


Fig. 1. Schematic diagram of the oxygen extraction cell.

(b) Teflon-bonded electrodes. The electrocatalyst was mixed with ICI GPI Fluon dispersion. The catalyst:Teflon ratio was usually fixed at 10:3. The mixture was then painted on to 100-mesh nickel screen and dried at 100°C for 1 hour, followed by final curing at 300°C in air for 1 hour. The catalyst loading was obtained from the difference in weight between the uncoated and the coated nickel screen.

4.3. Experimental methods

The oxygen extraction cell consisted of three glass compartments containing 5M KOH as the electrolyte (Fig. 1). A Teflon-bonded cathode was used in the floating mode [11] in the first compartment. The tip of the Luggin capillary was placed about 1 mm below the floating electrode and a dynamic hydrogen reference electrode (DHE) was used to monitor the potential of the working electrode. A piece of Teflon-bonded CoFe_2O_4 , supported on a nickel screen or a NiCo_2O_4 -coated screen in the second compartment, served as the peroxide decomposition assembly. In the third compartment, a Teflon-bonded NiCo_2O_4 electrode was used as the anode. Potentiostatic or galvanostatic control was provided by a Chemical Electronics potentiostat. A gas burette attached to the top of the second and third compartments was used to measure the amount of oxygen produced. A thermostatted Pyrex glass reaction vessel with a

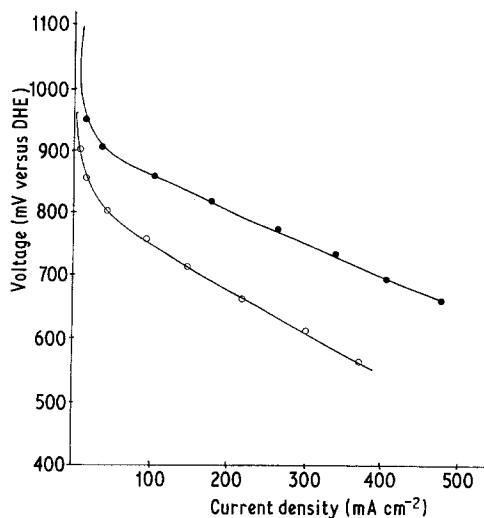


Fig. 2. Steady-state measurement of oxygen reduction. ●, On Teflon-bonded platinum black electrode (catalyst loading 16.1 mg cm⁻²); ○, on Teflon-bonded graphite electrode (catalyst loading 14.5 mg cm⁻²). 5 M KOH in air at 25° C; *iR* corrected.

gas burette attachment [5] was used in the H₂O₂ decomposition studies.

5. Results and discussion

5.1. Steady-state performance

Fig. 2 shows the *iR*-free performance of a Teflon-bonded graphite electrode as well as a Teflon-bonded platinum black electrode for the reduction of oxygen in 5 M KOH in air at room temperature. This shows that at any practical current densities, the platinum black electrode is only about 150 mV better than the graphite electrode. Fig. 3 compares the anodic performance of Teflon-bonded platinum black and NiCo₂O₄ electrodes. As expected, NiCo₂O₄ is significantly more active than platinum black [10], since the redox potential of the lower-NiCo₂O₄/higher-NiCo₂O₄ couple (~ 1.45 V) is far lower than the PtO/PtO₂ couple (~ 1.70 V).

5.2. Peroxide production

Teflon-bonded graphite electrodes were operated as air cathodes at fixed current densities for 1 hour. The cathode and anode were separated by No. 4 glass frit in a two-component cell, thermostatted at 25° C. A piece of 8 cm² Teflon-bonded

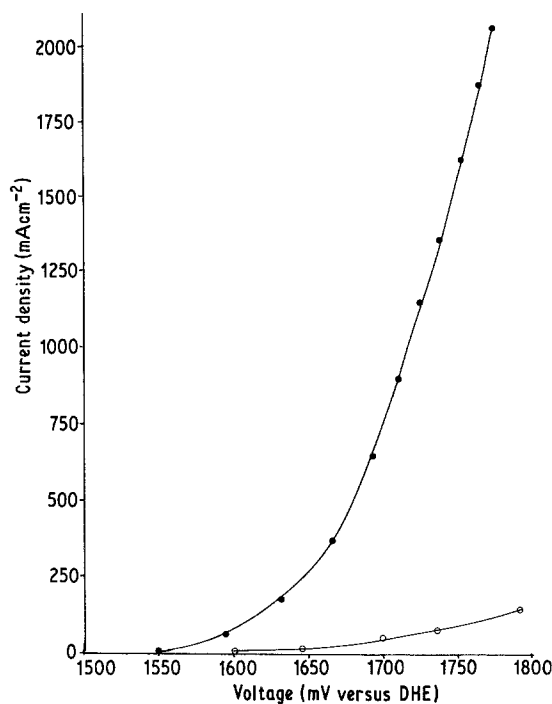


Fig. 3. Steady-state measurement of oxygen evolution on Teflon-bonded platinum black and NiCo₂O₄ electrodes. ●, Oxygen evolution on Teflon-bonded NiCo₂O₄ electrode (on Ni screen), catalyst loading = 14 mg cm⁻²; ○, oxygen evolution on Teflon-bonded platinum black electrode (on Pt screen), catalyst loading = 22.1 mg cm⁻². 5 M KOH in air at 25° C; *iR* corrected.

graphite electrode was used in the floating position in the cathode compartment (volume of electrolyte: 80 cm³, distance from the centre of the cathode to glass frit: ~ 6 cm). An air pump was used to supply air to the cathode compartment. A 20 cm², 100-mesh nickel screen was used as the counter electrode. A Chemical Electronics potentiostat (TR 40-3A) was used to feed current into the cell. After 1 hour, the concentration of H₂O₂ in the 5 M KOH solution was measured by titrating the acidified, ice-cooled solution with standard potassium permanganate solution. The self-decomposition of hydrogen peroxide in 5 M KOH in the same apparatus and under similar experimental conditions (but without passing current) was measured and found to be 0.525 g l⁻¹ of HO₂⁻ per hour.

Table 1 shows the amount of HO₂⁻ produced after the passage of a fixed amount of current for 1 hour. This confirms that the reduction of oxygen on graphite surfaces proceeds via the Berl mechan-

Table 1. Hydrogen peroxide produced from O_2 reduction on a 8 cm^2 Teflon-bonded graphite electrode. Current passed through cell for 60 min

Current (mA)	Theoretical (g HO_2^-)	Experimental average (g HO_2^-) (in 80 cm^3 electrolyte)	Experimental/theoretical (%)
200	0.1230	0.0917	74.55 (2)
400	0.2460	0.1866	75.85 (2)
600	0.3693	0.2675	72.40 (2)
800	0.4924	0.3575	72.6 ± 0.02 (4)

ism [4]. The amount of HO_2^- in the cathode compartment was only about 74% of the total amount of HO_2^- produced. This is mainly caused by the decomposition of HO_2^- on the nickel oxide anode surface. This loss has not been measured in our blank correction. In addition, there is some additional decomposition of H_2O_2 during the pipetting of the solution and the titration operation.

5.3. Kinetics of H_2O_2 decomposition

Two types of peroxide decomposition catalysts were evaluated: $CoFe_2O_4$ and $NiCo_2O_4$. Goldstein and Tseung [5] have shown that $CoFe_2O_4$ is very

active for H_2O_2 decomposition, since the greatest availability of Co^{II} occurs at this composition. No work has been reported on the activity of $NiCo_2O_4$ for H_2O_2 decomposition but since the highest availability of Co^{II} [12] also occurs at this composition in the nickel/cobalt oxide series, it was chosen for further evaluation. Fig. 4 shows a $\log_{10}[1 - (c/a)]$ versus t plot for freeze-dried $NiCo_2O_4$ (BET surface area $69.7\text{ m}^2\text{ g}^{-1}$), where a is the initial H_2O_2 concentration and c is the amount of H_2O_2 which has reacted at time t . The plot is linear over 95% of the total reaction time. Moreover, the rate constant for the reaction was shown to be independent of the initial H_2O_2 concentration but directly proportional to the catalyst mass

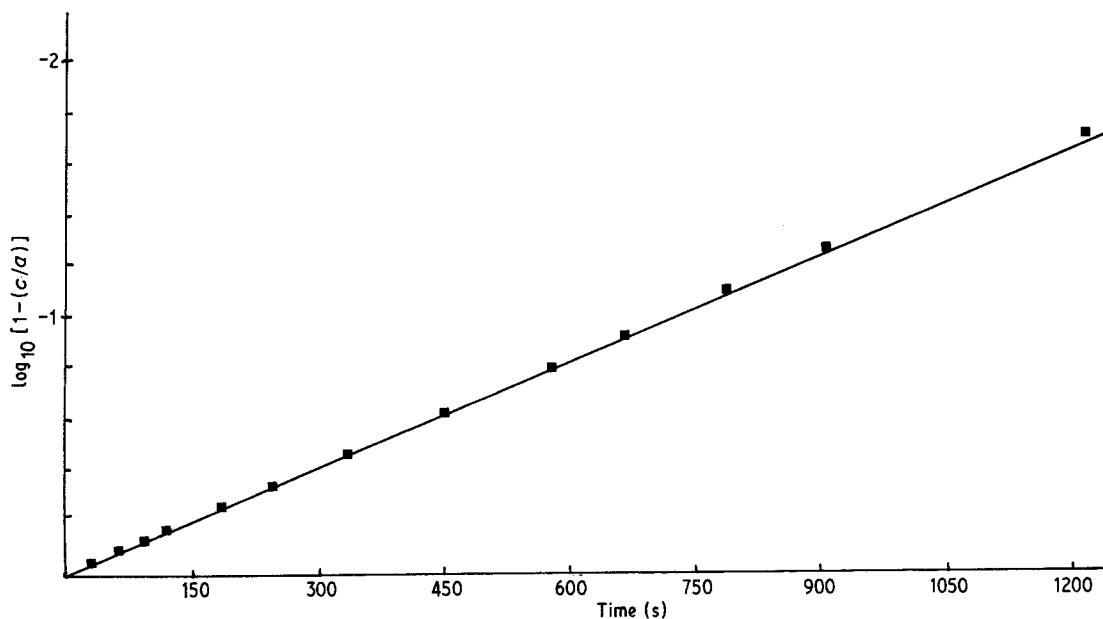


Fig. 4. $\log_{10}[1 - (c/a)]$ versus t showing first-order kinetics for H_2O_2 decomposition at 25°C by $NiCo_2O_4$ powder (prepared by freeze drying). a = initial concentration of $H_2O_2 = V_0 - V_\infty$; c = amount of H_2O_2 which has reacted at time $t = V_0 - V_t$ (V_0 = burette reading at zero time, V_t = burette reading at time t , V_∞ = burette reading at infinite time). First-order rate constant $K_{t,m} = 4.44 \times 10^{-2}\text{ s}^{-1}\text{ g}^{-1}$.

Table 2. First-order rate constant per unit mass of catalyst ($K_{f,m}$) for H₂O₂ decomposition

Catalyst	$K_{f,m}$ (10 ⁻² s ⁻¹ g ⁻¹)	Temperature (°C)
NiCo ₂ O ₄ powder (freeze dried)	4.44	25
	6.30	30
	7.40	35
	10.24	40
4 cm ² Teflon-bonded NiCo ₂ O ₄ electrode (on Ni screen)	0.24	25
4 cm ² porous NiCo ₂ O ₄ electrode (thermal decomposition of nitrates on Ni screen)	4.80	25
CoFe ₂ O ₄ powder (hydroxide precipitation method)	18.28	25

in the reaction mixture. These results are characteristic of first-order kinetics. Experiments were also conducted at 30, 35 and 40°C. By plotting the first-order reaction rate constant $K_{f,m}$ against $1/TK$, the activation energy for the decomposition of H₂O₂ over NiCo₂O₄ was found to be 10.98 kcal mol⁻¹, similar to the value of 10.60 kcal mol⁻¹ obtained by Goldstein and Tseung for the decomposition of H₂O₂ on CoFe₂O₄. Table 2 lists the $K_{f,m}$ values for NiCo₂O₄ powder (prepared by freeze drying), the Teflon-bonded NiCo₂O₄ electrode, porous NiCo₂O₄ on a nickel screen (prepared by thermal decomposition of cobalt and nickel nitrates on Ni screens at 400°C for 10 hours), as well as CoFe₂O₄ [13] prepared by coprecipitation of cobalt iron hydroxides, followed by dehydroxylation at 100°C (BET area: 120 m² g⁻¹).

This shows that CoFe₂O₄ is more active than NiCo₂O₄. However, taking into account the differences in surface area, their activity per unit area is similar. In addition, if CoFe₂O₄ was used in an actual cell, it had to be either fired on to nickel screens or bonded with Teflon; both processes require 300–400°C heat treatment and the surface area of the co-precipitated CoFe₂O₄ is reduced significantly.

It is interesting to note that the activity of the porous NiCo₂O₄ electrode for H₂O₂ decomposition is also double the activity of the Teflon-bonded NiCo₂O₄ electrode. This is not surprising since the oxygen produced inside the pores of the electrode will push the electrolyte out of the pores and most

of the catalytic reaction will occur on the electrode surface. Approximately 50% of the Teflon-bonded electrode surface is composed of Teflon particles and hence its activity for H₂O₂ decomposition is expected to be lower. In addition, the presence of hydrophobic Teflon particles reduces the rate of diffusion of electrolytes. Therefore, porous NiCo₂O₄ on a nickel screen was chosen as the H₂O₂ decomposition assembly.

Table 3 shows that the best results were obtained when graphite was used as the cathode and a piece of NiCo₂O₄ supported on a nickel screen was placed between the cathode and NiCo₂O₄ anode (cells A and B). When no separate H₂O₂ decomposing assembly was used (cell C), the power consumption was similar to a cell which used platinum black as the cathode (cell D). Even though the cathodic reduction of oxygen on graphite proceeded via a two-electron process with the formation of HO₂⁻, the peroxide ions which had diffused to the anode compartment were not fully decomposed; when the power was switched off in cell C, gassing continued slowly for a long time on the Teflon-bonded NiCo₂O₄ surface which is not as active as the thermally decomposed NiCo₂O₄ used in the H₂O₂ decomposition assembly. This suggests that when the anode is functioning electrochemically, the oxygen bubbles evolved effectively blanket a large part of the surface, making it unavailable for the HO₂⁻ decomposition reaction (cell C). On the other hand, when an H₂O₂ decomposition assembly was placed between the platinum cathode and the NiCo₂O₄

Table 3. Extraction of oxygen from air (400 mA passed through cell for 30 min)

Cell	Temperature (°C)	Cathode	H ₂ O ₂ decomposer	Anode	Theoretical		Experimental (cm ³ NTP)	Voltage (V)	Power consumption (kW h l ⁻¹ O ₂)
					From H ₂ O ₂ decomposition (cm ³ NTP)	From O ₂ evolution (cm ³ NTP)			
A	25	4 cm ² Teflon-bonded graphite on nickel screen	2 × 10 cm ² NiCo ₂ O ₄ on nickel screen	4 cm ² Teflon-bonded NiCo ₂ O ₄ on nickel screen (O ₂ evolving)	45.60	45.60	78.03 ± 3.18[5]	1.34	3.46
B	40	Ditto	Ditto	Ditto	45.60	45.60	77.04 ± 3.02[4]	1.04	2.69
C	25	Ditto	None	Ditto	N/A	45.60	49.82 ± 1.11[3]	1.34	5.41
D	25	4 cm ² Teflon-bonded Pt black on Pt screen (O ₂ reduction)	None	Ditto	N/A	45.60	46.96 ± 0.68[5]	1.26	5.36
E	25	Ditto	2 × 10 cm ² NiCo ₂ O ₄ on nickel screen	Ditto	N/A	45.60	47.77	1.26	5.26
F	25	4 cm ² Teflon-bonded Pt black on Pt screen (H ₂ evolving)		Ditto	N/A	45.60	45.80	2.09	9.12
G	40	Teflon-bonded Pt electrode (O ₂ reduction)		Teflon-bonded Pt electrode (O ₂ evolving)	N/A	45.60	45.60	1.0	4.38

anode, there was no improvement. This is not surprising, since most of the HO₂⁻ produced at the platinum cathode surface would be decomposed, yielding O₂ for further cathodic reduction [6] (cell E). It is interesting to note that in all cases, the power consumption is significantly lower than a conventional water electrolyzer (cell F). Moreover, cell B is significantly better than the results obtained by Wynveen and Montgomery [2] (cell G), which used platinum black anode and cathode.

It is important to note that not all the HO₂⁻ produced by the graphite cathode has been utilized in our experimental cell. This is mainly caused by the large separation between the cathode and the anode and is not due to the difference in the diffusion coefficient between HO₂⁻ ($\sim 9.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [14] and OH⁻ ($\sim 0.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [15]. This can be remedied by decreasing the cathode/anode gap in future designs, in a similar manner to that of Wynveen and Montgomery [2].

6. Conclusions

The principle of an inexpensive and efficient oxygen extractor based on an integrated electrochemical-chemical method has been demonstrated. This oxygen extractor is particularly suitable for village clinics in developing countries where bottled oxygen is not readily available. Other specialized applications include oxygen supply for fighter pilots and military field hospitals.

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