An oxygen-releasing device: reversible oxygen release from a cobalt chelate–carbon composite in response to an applied voltage

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A disk (*e.g.* diameter 2 cm × 2 mm) was made of [*N*,*N*′-bis(salicylidene)ethylenediamine]cobalt [Co(salen)] and carbon powder. The composite disk selectively absorbed oxygen from air, *e.g.* 22 cm^3 oxygen per gram of composite at room temperature, which is almost stoichiometrically ascribed to 2 : 1 cobalt–dioxygen adduct formation. The adduct formation was an exothermic reaction, and the absorbed oxygen was released above 80 °C. The application of 6 V to the disk sandwiched between platinum meshes induced a temperature elevation in the disk, which quickly released the absorbed oxygen. Under ambient conditions, the oxygen-releasing and -absorbing processes could be established within a few min and a 30 min interval, respectively, for the composite disk containing the 3-ethoxy derivative of Co(salen), while the oxygen absorption took several hours for the Co(salen) disk.

[*N*,*N*′-Bis(salicylidene)ethylenediamine]cobalt [Co(salen)] and its derivatives are the oldest known examples of oxygen-carrying chelates.[1,2] Even in the solid state, Co(salen) in the air forms a 2 : 1 Co–dioxygen adduct, as represented in eqn. (1).

$$\mathrm{Co(salen)} + \mathrm{O_2} \rightleftharpoons \mathrm{(salen)Co{-}O_2{-}Co(salen)} \qquad (1)$$

This oxygen-adduct formation is reversible in response to atmospheric oxygen pressure, and is enhanced at lower temperature; the oxygen absorption is an exothermic reaction with an enthalpy gain of *ca.* 125 kJ mol^{-1}.[2]

We have been studying oxygen-carrying metal complexes,[3] such as metalloporphyrins and cobalt Schiff base chelates such as Co(salen), and developing them as red cell substitutes[4] and as oxygen-permselective membranes.[5] This paper describes, for the first time, an oxygen-releasing device, which has been successfully prepared by the formation of a composite of the oxygen-carrying but electrically insulating Co(salen) and conductive carbon powder.

Experimental

Co(salen) and [*N*,*N*′-bis(3-ethoxysalicylidene)ethylenediamine]cobalt [Co(Esalen)] were synthesized according to the published methods.[1,2] Co(salen) and Co(Esalen) were recrystallized from pyridine and heated at 170 °C *in vacuo* for 1 day to completely remove the pyridine. The Co(salen) and Co(Esalen) crystals were ground, then sieved into a narrow particle size range (40–50 μm). Electrically conductive carbon powder (Fujikura Chemical Co., Japan; carbondotite, specific gravity 0.9–1.0) was washed several times with hexane, dried *in vacuo*, and sieved into the size range 40–50 μm. The Co(salen) (0.5 g) and the carbon (0.3 g) were mixed, sandwiched between platinum meshes, and pressed under 120 kg cm^{-2} pressure for 3 min, to yield Co(salen)–carbon disk (diameter 2 cm, thickness 2 mm). Copper wires were connected to the center of the platinum meshes and a voltage was applied to them. The electrical resistance and temperature of the disk under the applied voltage were measured with a multitester and a thermister thermometer, respectively.

The disk was put into a 100 cm^3 vessel at a constant pressure of 1 atm and heated using a thermocontrolled bath or an applied voltage. The amount of oxygen absorbed onto or released from the disk was measured with an oxygen sensor (Koumei Co., Japan, OM-511). The amount of absorbed oxygen was also measured by the pressure decrease in a constant volume using a Baratron absolute pressure gauge (MKS Instruments, USA). The apparatus consisted of a vacuum line mounted in a thermocontrolled air bath. The cobalt distribution in the disk was measured using an X-ray microanalyzer (Hitachi S-570). Oxygen-adduct formation of the Co(salen) composite in the disks was measured using a VIS–NIR spectrophotometer (Shimadzu UV-3101PC) equipped with a reflectance apparatus.

Results and Discussion

Homogeneous mixing of Co(salen) and carbon was recognized by the homogeneous deep red–brown color of the broken pieces of the disk and by the homogeneous Co distribution in the disk as determined by X-ray microanalysis. The disk was not mechanically tough but remained intact during the following repeated temperature elevation and depression (80 °C to room temp.) or oxygen-releasing and -absorbing tests.

A 6 V potential (4 dry cells connected in series) was applied to the disks with various compositions of Co(salen) and carbon. Table 1 shows the electrical resistance and heat elevation of the disks. Although the disks containing >80% Co(salen) had excessively high electric resistances, the disks containing *ca.* 70% Co(salen) possessed moderate conductivity enabling them to raise the temperature while maintaining the Co(salen) or oxygen absorption capability. These disks exhibited an electrical resistance of 3 Ω and a temperature elevation of *ca.* 80 °C with an applied voltage of 6 V.

The 71% Co(salen)–carbon composite disk absorbed 22 cm^3 oxygen per gram of composite at room temperature (Fig. 1). The mole ratio of the amount of absorbed oxygen to the Co(salen) in the composite was 0.49, which corresponds to stoichiometric oxygen binding represented in eqn. (1). The

Table 1 Electrical resistance and heat elevation upon the application of 6 V to the Co(salen)–carbon disk

Co(salen) (wt.%)	R/Ω	$T/^\circ\mathrm{C}$
100	∞	25
83	2000	26
77	34	55
71	3	83
67	2	50

Disk: diameter 2 cm × 2 mm, 20 min application of 6 V, room temp. = 25 °C.

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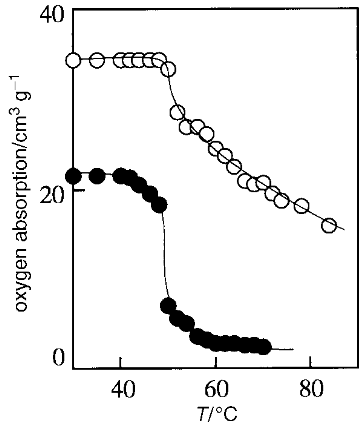

Fig. 1 Oxygen absorption with the 71% Co(salen)–carbon disk (●) and the Co(salen) disk (○)

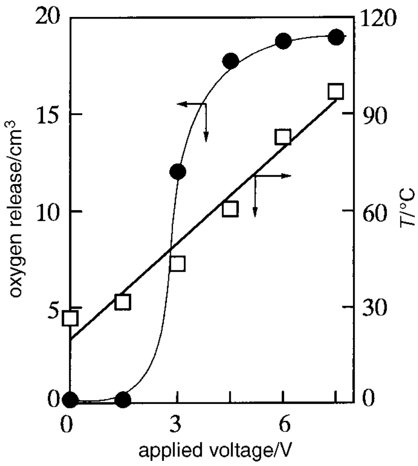

Fig. 2 Effect of applied voltage on oxygen release (●) and temperature (□) for the Co(salen)–carbon (0.5 g/0.3 g) disk

oxygen-binding affinity was reduced or the absorbed oxygen was released when the thermobath temperature was increased, and the oxygen release was complete at *ca.* 75 °C for the composite disk. On the other hand, the 100% Co(salen) disk released oxygen at a higher temperature. The formation of a composite with carbon caused a side effect or a positive effect on the oxygen release, probably because the added carbon compensates for a structural change in Co(salen) caused by the oxygen-binding solid-state reaction.

The steady-state temperature of the 71% Co(salen)–carbon composite disk increased with the voltage applied to the disk, and reached 80 °C with the application of 6 V (Fig. 2). In response to the temperature elevation, the disk released oxygen, *e.g.*, 22 cm^3 oxygen per gram of composite or, *e.g.*, 18 cm^3 per disk (diameter 2 cm × 2 mm), with application of 6 V.

VIS–NIR reflectance spectra of the Co(salen)–carbon disk were measured both with and without an applied voltage. The spectrum of the disk with no applied voltage was characterized by a strong absorption in the visible and near-IR regions (see Fig. 3, inset). The spectrum changed with the voltage application to give a peak at 1190 nm, which has been assigned to deoxy-Co^{II}(salen).[6] This spectral change was reversible in response to the applied voltage. The fraction of oxygen adduct formed is plotted in Fig. 3, which coincides with the oxygen release profile upon the voltage application given in Fig. 2.

The oxygen release with the application of 6 V, and the oxygen absorption with no applied voltage could be repeated more than 100 times for the 71% Co(salen)–carbon disk

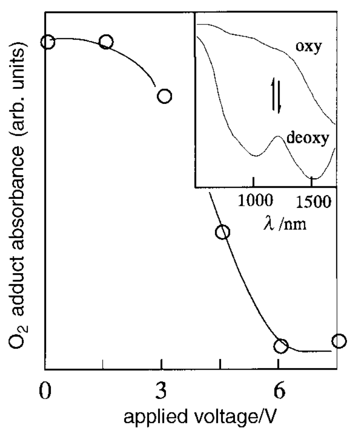

Fig. 3 Effect of applied voltage on oxygen-adduct formation for the Co(salen)–carbon disk. Inset: near-IR reflectance spectra of Co(salen).

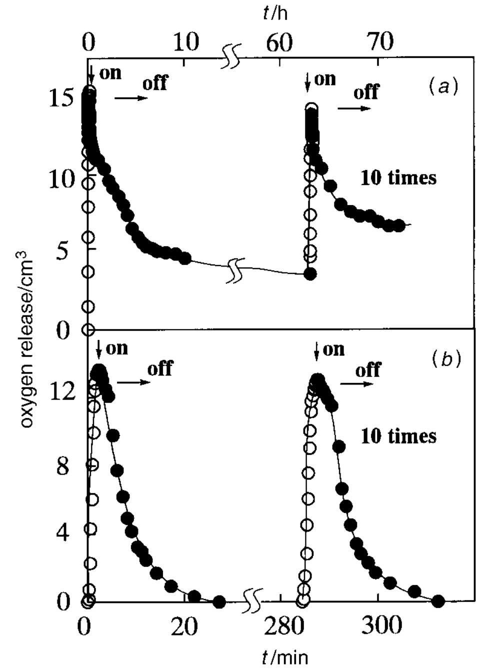

Fig. 4 Oxygen-releasing cycle for the Co(salen)–carbon disk (*a*) and the Co(Esalen)–carbon disk (*b*); (○) 6 V application, (●) voltage off.

[Fig. 4(a)]. The former was completed within a few minutes, but the latter took several hours. The corresponding carbon composite disk of Co(Esalen) was also prepared. This 62% Co(Esalen)–carbon disk released oxygen (*ca.* 18 cm^3 per gram of composite) with 6 V applied and absorbed oxygen rapidly in the absence of an applied voltage. The oxygen-releasing and -absorbing cycle is shown in Fig. 4(b); the cycle could be repeated, with a 30 min switching on–off interval, more than 100 times. The oxygen release and absorption were not influenced by the presence of carbon monoxide, carbon dioxide or 80% humidity.

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