Structures and Properties of Modified Ethylcellulose Oxygen-Enriched Membranes

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INTRODUCTION

We have attempted to use complex formation to prepare ethylcellulose-cobalt (II) acetate tetrahydrate [EC–Co(Ac)$_2$] and ethylcellulose-bis(salicylaldehyde)-*o*-phenylenediamine cobalt (II) [EC–Co(Salphen)] composite oxygen-enriched membranes and to improve the low gas permeabilities of EC membrane. The performance of the membranes was measured by the constant-pressure volumetric method with compressed air as feed. The oxygen-enriched air permeabilities of EC membrane are significantly improved, and the selectivity of EC membrane is slightly decreased, by adding the metal salt cobalt (II) acetate tetrahydrate [$Co(Ac)_2 \cdot 4H_2O$] to EC macromolecules. For example, the oxygen-enriched air permeability and oxygen content of the composite membrane EC–Co(Ac)$_2$ are 17.9 bar and 30.7%, respectively; however, the oxygen-enriched properties of the EC membrane are raised by adding the metal cobalt complex compound Co(Salphen) to the EC membrane. For instance, the oxygen-enriched air permeability and oxygen content of the composite membrane EC–Co(Salphen) are 17.4 bar and about 40%, respectively. From the morphology and infrared spectra, we find that the improvement of the oxygen-enriched air permeabilities for the modified EC membrane is due to the complex formation of the EC–Co(Ac)$_2$ and EC–Co(Salphen) composite membranes. Additionally, since the effects of operating temperature on the oxygen-enriched performances (i.e., both oxygen-enriched air permeabilities and selectivities of the composite membranes increase with the enhancement of operating temperature) are different from that for the EC membrane further demonstrates the existence of the complex formation in the composite membranes.

Since oxygen-enriched air with an oxygen content of 30–40% is of great value, it is becoming attractive. Oxygen-enriched air can be applied in many fields (e.g., combustion, medical treatment, and as a way of improving the efficiency of transportation modes). When the oxygen-enriched air is used in combustion processes, it greatly raises the efficiency of combustion equipment, which helps to save energy and resources and also to protect the environment. Producing oxygen-enriched air requires membranes with higher oxygen-enriched air permeability and the highest possible selectivity. So far the following three methods have been used to produce oxygen-enriched air: croygenic distillation, absorption, and membrane separation. Of these three ways, membrane separation is taken seriously because of its advantages, such as lower energy expenditure, lower cost, and easier operation. With the advancement of membrane technology, various oxygen-enriched membranes made from different materials have been developed. Cellulose and its derivates are usually used as the basic materials for oxygen-enriched membranes that produce oxygen from air because (1) these raw materials are readily obtainable, (2) their cost is low, (3) they can be used to prepare membranes easily, and their (4) membrane-forming properties are good.[1–4]

To our regret, however, the oxygen-enriched air permeabilities of these membranes are still a little low. To improve the gas permeability of ethylcellulose membranes, we carried out blend-modifications by adding Co(Ac)$_2$ or Co(Salphen) to ethylcellulose. The results were just as we expected. Although there have been some reports on the enhancement of membrane air permeability,[5–7] these studies have only discussed the permeabilities of pure oxygen and nitrogen in membranes, and did not address practical oxygen-enriched performances and the structure of the membranes. We have therefore made a series of detailed studies on the structures and the practical oxygen-enriched properties of the modified membranes.

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EXPERIMENTAL

Materials

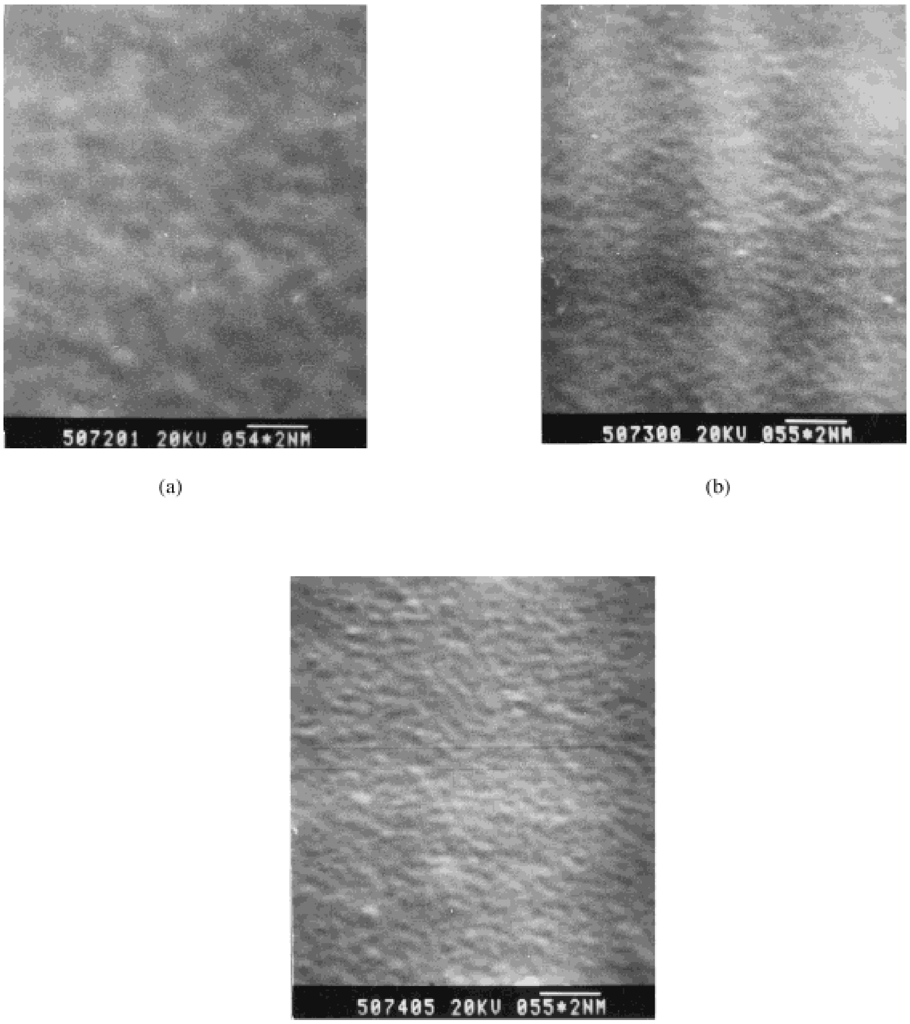
Ethylcellulose for use as membrane raw material was purchased from Shantao Xinning Chemical Works in Guang Dong Province in P.R. China. The viscosity of ethanol–methybenzene solution of 5% ethyl-cellulose is about 0.05 Pa.s. The cobalt (II) acetate tetrahydrate [$Co(Ac)_2 \cdot 4H_2O$)] and chloroform used were analytically pure. The bis(salicylaldehyde)-*o*-phenylenediamine) cobalt (II) [Co(Salphen)] was synthesized in the laboratory. The elemental analysis showed C: 64.71; H: 3.80; N: 7.64 (the calculated elemental analysis revealed C: 64.35; H: 3.79; N: 7.51).

Preparation of Membranes

The membranes were prepared by the dry-phase inversion method. The casting solutions were cast on a clean glass plate under an atmosphere free of air and then were evaporated for 2 days to yield the flexible membranes with thickness of about 30 μm.

Structures of Membranes

The chemical structures of membranes were analyzed by infrared spectroscopy. The morphology of the membranes were observed under a JEM-1200 EXIS type of



(c)

Figure 1 SEM surfaces of oxygen-enriched membranes prepared. (a) EC membrane (b) EC–$Co(Ac)_2$ composite membrane (c) EC–Co(Salphen) composite membrane.

scanning electron microscope made by the Japanese Electron Light Company.

Measurements of the Properties of Membranes

The permeabilities of membranes were determined by the constant-pressure volumetric method with compressed air as feed. The oxygen content was estimated using the pyrogallic acid absorption method. These methods have been introduced in the literature.[8]

RESULTS AND DISCUSSION

The morphology of the composite membranes [Fig. 1(a–c)] shows that there are less polymer aggregates (often referred to as nodules[9]) on the EC-membrane surface than on the surfaces of the EC–Co(Ac)$_2$ or EC–Co(Salphen) membranes. As shown in Figure 2(a), the cross section of the EC membrane consists of an ultrathin, dense skin layer supported by a coarse, spongelike, macrovoid-free structure. A comparison of the EC membrane with the EC–Co(Ac)$_2$ membrane reveals that the dense skin layer of the cross section of the membrane with the added metal salt is much thinner and that large macrovoids are present in the cross-sectional layer. The membrane with the added metal complex compound (i.e., the EC–Co(Salphen) composite membrane), however, has a dense, spongelike cross section with an essentially macrovoid-free structure. Thus we may hypothesize that the addition of the metal salt Co(Ac)$_2$ to EC would increase the oxygen-enriched

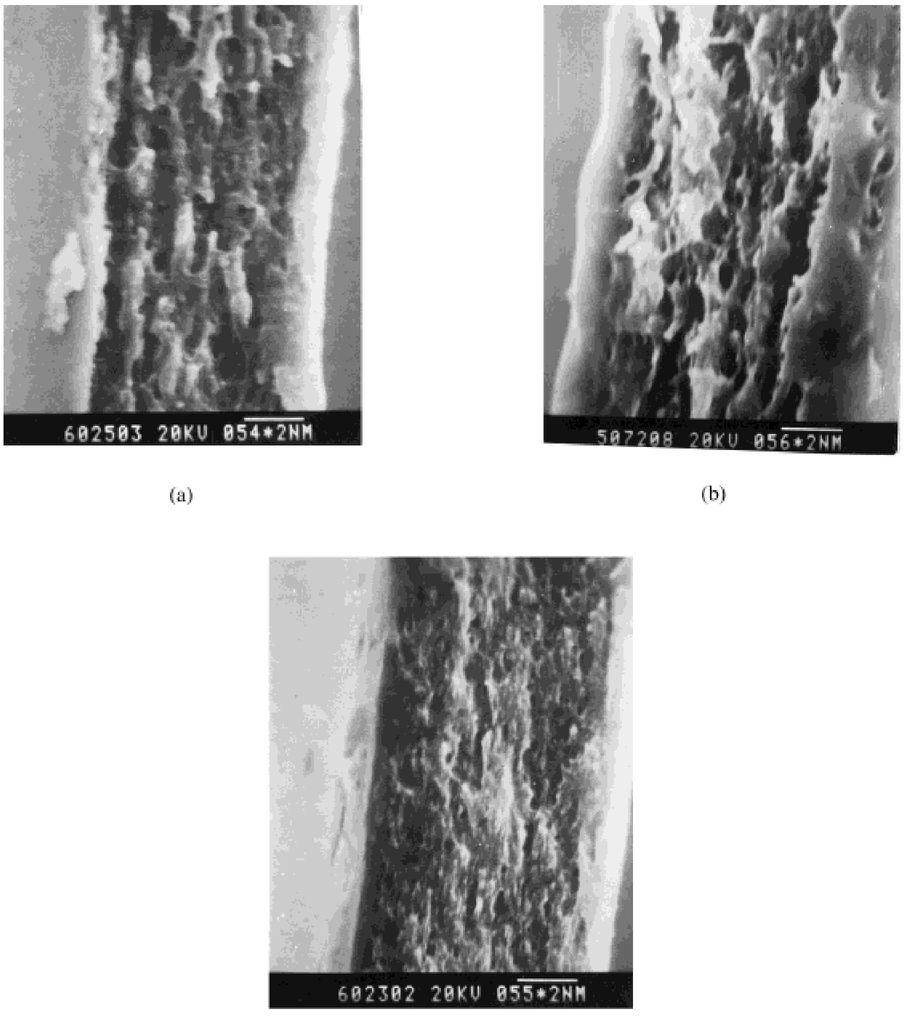


Figure 2 SEM cross-section structures of oxygen-enriched membranes prepared. (a) EC membrane (b) EC–Co(Ac)$_2$ composite membrane (c) EC–Co(Salphen) composite membrane.

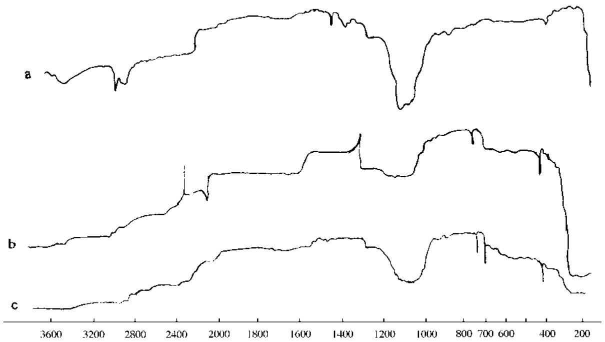


Figure 3 Infrared spectra of EC (a). EC–Co(Ac)$_2$ (b) and EC–Co(Salphen) (c) membrane.

air permeability, whereas the addition of the metal complex compound to EC could improve the selectivity of the EC membrane.

The Complex Formation of the Modified Membranes

Infrared studies were made to examine the existence of complex formations of the modified membranes. The infrared spectra of the EC, EC–Co(Ac)$_2$, and EC–Co-(Salphen) membranes are illustrated in Figure 3. Additional strong absorption peaks appear in the spectra of the EC–Co(Ac)$_2$ and EC–Co(Salphen) membranes, which is assigned to the EC and Co(Ac)$_2$ or EC and Co(Salphen) coordination. This result suggests the complex formation of the EC–Co(Ac)$_2$ or EC–Co(Salphen) membrane. The ether-link absorption bands in the spectra of the composite membranes are irregular and shift towards much lower wave bands. In addition, another strong absorption band appears in the spectra of EC–Co(Ac)$_2$ or EC–Co(Salphen) membrane at about 420 cm^{-1}, which can be attributed to the absorption peak of Co–O$_2$ caused by the absorption of cobalt by oxygen.

Oxygen-Enriched Properties of The Membranes

The oxygen-enriched performances of the membranes are summarized in Table I. These results show that the oxygen-enriched air permeability of the EC membrane is significantly improved by modification (i.e., by adding the metal salt or metal complex compound). The oxygen-enriched air permeability of the EC–Co(Ac)$_2$ membrane is the highest, but its selectivity is the lowest. The oxygen-enriched air permeability of the EC–Co(Salphen) membrane is medium, whereas the selectivity is superior. From these results, we concluded that the addition of Co(Ac)$_2$ could enhance the permeability and that the addition of Co(Salphen) could raise the oxygen content (i.e., selectivity of the membrane for O_2–N_2). This result is in agreement with the microscopic analysis. It is important to note that the oxygen-enriched performance of the EC–Co(Salphen) membrane is superior to that of the EC membrane in contradiction to their structures. This can be due to the complex formation of the polymer EC with the cobalt complex compound Co(Salphen), which changes the permeative mechanism of oxygen in the membrane from a solution–diffusion mechanism to a dual-absorption one (i.e., the Henry and Langmuir absorption of oxygen in complex).[5,6,10,11]

It is interesting to note that the permeability of EC membrane rises but that the oxygen content decreases as the operating temperature is raised, whereas the permeability and selectivity of either EC–Co(Ac)$_2$ or EC–Co(Salphen) membrane simultaneously increase (Table I). This could be explained by hypothesizing that the complex formation of polymer EC with either Co(Ac)$_2$ or Co(Salphen) results in a profound change in the permeative mechanism of air in the composite membranes. It was, however, unexpected that the addition of Co(Ac)$_2$ would lower the selectivity of the EC membrane. The inorganic salt Co(Ac)$_2$ can lead to the emergence of pores during preparation of ultrafiltration membranes. As a result, we could infer that the introduction of Co(Ac)$_2$ causes defects to develop in the composite membrane, which we can observe from the cross section of the EC–Co(Ac)$_2$ membrane. Hence, the selec-

Table I Measured Oxygen-Enriched Performances of EC Membranes and of EC–Co (Ac)$_2$ and EC–Co (Salphen) Composite Membanes

	30°C		40°C		50°C	
Membranes	P_{OEA}[a]	Y_{O_2}[b]	P_{OEA}	Y_{O_2}	P_{OEA}	Y_{O_2}
EC	5.6	35.0	8.3	34.6	12.1	34.0
EC–Co (Ac)$_2$	12.7	27.3	16.7	29.3	17.9	30.7
EC–Co (Salphen)	9.2	36.7	12.6	38.1	17.4	39.6

[a] bar, 1 bar = 10^{-10} cm^3 (STP) cm/cm^2 × s × cmHg.
[b] Y_{O_2}: mol %.

tivity of the EC–$Co(Ac)_2$ membrane can not be improved despite the complex formation. However, the addition of $Co(Ac)_2$ can greatly enhance the oxygen-enriched air permeability of the EC membrane.

CONCLUSIONS

The oxygen-enriched air permeability of the EC membranes are significantly improved by adding metal cobalt salt or metal cobalt complex compound to modify the EC membrane. The oxygen-enriched air permeability and oxygen content of an EC membrane under the conditions of operating temperature at 50°C and the pressure difference of 0.5 MPa are 12.1 bar and 34.0%, respectively, those of the EC–$Co(Ac)_2$ membrane are 17.9 bar and 30.7%, respectively, and those of the EC–Co(Salphen) membrane are 17.4 bar and 39.6%, respectively. This indicates that the addition of $Co(Ac)_2$ can greatly increase the oxygen-enriched air permeability, but the addition of Co(Salphen) to an EC membrane can enhance not only the oxygen-enriched air permeability but also the selectivity. These improvements are due to the complex formation, which is verified by morphology and infrared spectra. Infrared analysis shows the existence of complex formations in the modified EC membranes. The oxygen-enriched air permeabilities and oxygen contents of either EC–$Co(Ac)_2$ or EC–Co(Salphen) membranes simultaneously rise as the operating temperature is raised. These results further verify the existence of complex formations in the modified EC membranes.

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