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Oxygen Permeation Through Composite Oxide-Ion and Electronic Conductors

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Oxygen permeation through composites consisting of four well-known oxide-ion conductors and a noble metal, Pd or Ag, is reported. The oxides were $Zr_{0.9}Y_{0.1}O_{1.95}$ (YSZ), $(Bi_{1.75}Y_{0.25}O_3)_{0.95}(CeO_2)_{0.05}$ (BYC5), $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SSC), and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM). The results show that (BYC5 + Ag) yields the highest oxygen permeation flux, but the composite deteriorates with time. The composites (SSC + Pd), (LSGM + Pd), and (YSZ + Pd) give stable, but relatively lower oxygen permeation flux in the order of (SSC + Pd) > (LSGM + Pd) > (YSZ + Pd). The composite microstructures indicate that (BYC5 + Ag) has the best percolating network for both oxide-ion and electronic pathways while (SSC + Pd) has the longest triple-phase boundary lengths with the smallest grains, which is beneficial to the surface oxygen exchange. It is shown that the microstructure of the composites, which strongly influences the competition between surface reaction and bulk diffusion, is technically as important as the oxide-ion conductivity. The activation energy appears to be related more to the morphology of the metallic phase than to that of the oxide phase. These results suggest that (SSC + Pd) is a promising composite mixed conductor for applications requiring oxygen separation.
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Electrochemical synthesis of syngas via ceramic membranes has been considered an economic and efficient alternative to transform natural gas into liquid fuel. The central component of this electrosynthesis is the oxygen-permeable ceramic membrane that is solely an oxide-ion and electronic conductor at high temperatures. The use of mixed conductors with both high oxide-ion and electronic conductivity assures a high oxygen permeation flux and a fast surface exchange rate. These membranes may be categorized into *(i)* homogeneous mixed oxide-ion and electronic conductors (MIECs) and *(ii)* composite oxide-ion electrolytes and metals. Most of the Co-containing single-phase perovskite oxides,[1-3] for example, are good MIECs that belong to the first category since both oxide ions and electrons inside these perovskites are mobile at elevated temperatures. A mixed oxide-ion and electronic conduction is also possible in a composite of an oxide-ion electrolyte and a noble metal if each component has a percolation pathway through the composite, a concept patented by Mazanec et al.[4,5] These composites function the same way as the MIECs. An immediate example is the oxide-ion conductor Y_2O_3-stablized ZrO_2 plus the noble metal Pd[6-9] that has been shown to have an appreciable oxygen permeation rate at elevated temperatures.

The relative advantages of each type of mixed conductor depend on the choice of materials and their preparations. Homogenous mixed conductors produce higher oxygen permeation flux, but those previously studied suffer degradation with time[2,3] due to either oxygen ordering or compositional alteration at the oxygen-lean side. Composite mixed conductors, on the other hand, can yield a stable oxygen permeation flux, but with a relatively lower oxygen permeation flux. From the commercial point of view, stability of the oxygen permeation is the most important criterion. Therefore, composite mixed conductors have been considered more attractive for industrial applications even though they are relatively costly.

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In this paper, we report measurements of oxygen permeation flux on composite mixed conductors consisting of the oxide-ion conductors $Zr_{0.9}Y_{0.1}O_{1.95}$ (YSZ), $(Bi_{1.75}Y_{0.25}O_3)_{0.95}(CeO_2)_{0.05}$ (BYC5), $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SSC), and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM), and a noble metal, either palladium or silver. The oxygen permeation fluxes of the above composites were measured with gas chromatography. The compositions and microstructures of the prepared composites were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

Experimental

Preparation of composites.—All the composites investigated in this study were made by solid-state reaction. The YSZ powders were purchased from the Tosoh Company, and all other oxide powders were made in our laboratory. The starting BYC5 powder was made by solid-state reaction after calcining at 700°C, while the starting SSC and LSGM powders were the products of decomposition at intermediate temperatures of polymer precursors made by a wet-chemical method. The details of the procedures are described in Ref. 10-12. The starting oxides had been thoroughly mixed with a required amount of PdO or silver powder. The mixtures were then pressed into 2.54 cm diam pellets before sintering at high temperatures. The sintering temperature for each composite is listed in Table I. At these temperatures PdO is reduced to elemental Pd.

X-ray diffraction and SEM.—The component phases and the reactivity between the oxides and Pd or Ag were examined with a powder X-ray diffractometer PW 1740. The powder diffraction was conducted from 10 to 80° with a Cu Kα target and Ni filter. The microstructure and elemental analysis of the as-prepared composites after polishing were observed with a JEOL 35C scanning electron microscope equipped with a Kevex energy dispersed spectrum system. In order to distinguish clearly the oxide and metal phases, a backscattered electron image was chosen.

Measurement of oxygen permeation.—The sintered composite pellets (~ 1.75 cm in diam) were ground on both sides with a diamond

Table I. Compositions and sintering temperatures of the composites.

	(BYC5 + Ag)	(SSC + Pd)	(LSGM + Pd)	(YSZ + Pd)
Oxide compositions	$(Bi_{1.75}Y_{0.25}O_3)_{0.95}(CeO_2)_{0.05}$	$Ce_{0.8}Sm_{0.2}O_{1.9}$	$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$	$Zr_{0.9}Y_{0.1}O_{1.95}$
Composite Compositions (oxide:metal)	60:40	66:34 60:40 50:50	60:40	60:40
Sintering temp (°C)	900	1450	1450	1450
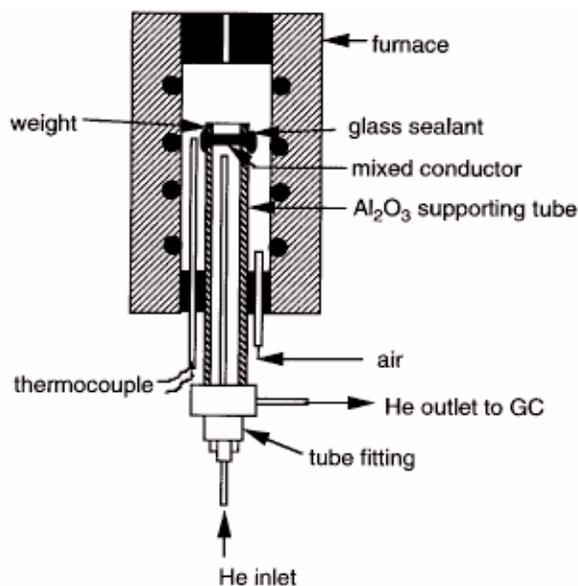
Figure 1. Experimental setup for oxygen permeation measurements.

Figure 2. XRD patterns of the studied oxide-metal composites.

wheel into a desired thickness. The grinding also assures removal of contaminated surface layers. The fresh pellets thus obtained were then mounted on the top of a supporting alumina tube with a glass sealing ring that was covered with a glass powder slurry to insure further sealing. A weight Al_2O_3 ring (same size as the supporting tube) on the top of the sample was also used to keep the seals leaktight while maintaining the same permeation area on both sides of the sample. The whole setup is shown in Fig. 1. The assembly was then loaded into the constant temperature zone of a vertical furnace and slowly heated to 900-930°C (for BYC5 sample, 750°C) to allow the glass to soften and seal the assembly. For the BYC5 composite, a different glass powder with a lower softening point was chosen. The oxygen permeation flux was measured with a SRI 8610C gas chromatograph; helium that had been passed through a moisture trap was used as the carry gas at a fixed flow rate of 12 mL/min. Another helium source was used as the sample sweeping gas with a flow rate of 10 mL/min for all the studied samples; ambient air was the feeding gas. Any detectable nitrogen was regarded as leakage, and the corresponding oxygen content was subtracted from the measured value. If the leaking nitrogen concentration was above 0.1%, the measurement was discarded. The experiments proceeded in a cooling sequence in steps of 20°C from 900-930 to 750°C (for the BYC5 + Ag composite, from 750 to 600°C). Since preliminary measurements on the Pd-composite mixed conductors indicated a stable oxygen permeation flux, we chose several hours of equilibration time at each temperature for these composites.

Results and Discussion

X-ray diffraction.—The XRD patterns of composite mixed conductors (Fig. 2) show only the two phases: the oxide and the elemental palladium or silver. No extra phases were found, which indicates no reactivity occurred between the oxide and metallic phases at the sintering temperatures. This observation assures the absence of any unwanted insulating phase in the prepared composites.

Microstructual examinations.—The microstructures of the studied composites are shown in Fig. 3. An oxide matrix containing dispersed metallic particles appears to be the general feature of these composites. This observation is consistent with the designed composition containing 60 vol % oxide. Even though the oxide matrix is similar in each composite, the metallic phase exhibits different morphologies. For example, Fig. 3a and c show large Pd particles in the YSZ and LSGM matrix, but much smaller particles in the SSC matrix can be seen in Fig. 3b. It is believed that different wettings between oxides and metals lead to the variations in microstructure. It seems that the SSC phase prohibits the growth of the Pd particles
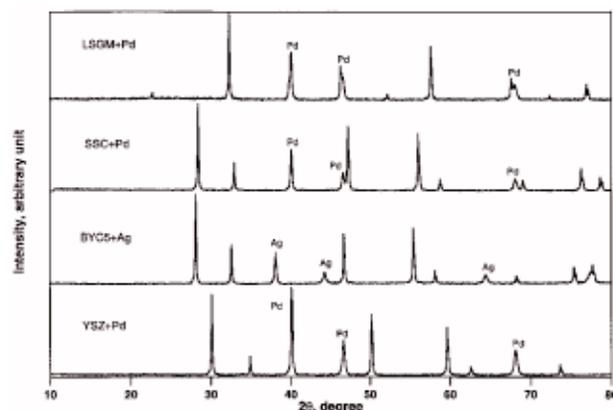
more efficiently than do the YSZ and LSGM phases. Small oxide and metal grains increase the triple-phase boundary lengths at the surface that are crucial for the exchange rate of oxygen and they aid formation of percolating pathways for both the oxide ions and the electrons, which further increases the oxygen permeation flux. The permeation measurements of Fig. 4 show a higher oxygen flux in the (SSC + Pd) composite compared to that of the (LSGM + Pd) composite even though the oxide-ion conductivity of the oxide phase is higher in LSGM than in SSC within the measuring temperature range. This finding demonstrates the importance of the microstructure of the composites. The microstructure of the (LSGM + Pd) composite (Fig. 3c) also shows some regions with dark color. Even though energy-dispersive spectroscopy (EDS) indicates a Ga-rich distribution in these regions, XRD does not show the presence of any extra phase. Further work is needed to clarify the composition and the role of these dark areas.

The microstructure of the (BYC5 + Ag) composite (Fig. 3d) shows both well-connected BYC5 and Ag networks, which ensures the simultaneous migration of oxide ions and electrons through their own percolation pathways. The low melting points of BYC5 and Ag and their wettability could contribute to the formed microstructure. Figure 4 indicates an oxygen permeation rate more than one order of magnitude higher in (BYC5 + Ag) than in the other composite mixed conductors even though the oxide ion conductivity does not differ that much. These results confirm the importance of establishing good percolation pathways for the metal as well as the oxide phase and indicate that wettability of the oxide and metal interfaces may provide an important parameter in the choice of an oxide-metal pair.

Oxygen permeation flux.—Oxygen permeation fluxes of different composite mixed conductors.—Figure 4 compares the measured oxygen permeation fluxes Jo_2 for the composite mixed conductors. The (BYC5 + Ag) composite shows a significantly higher Jo_2 than the other three composites; it possesses lower activation energy E_a and a better-networked microstructure as shown in Fig. 3d. Unfortunately, a slow decrease of Jo_2 with time was found at high temperatures. This probably results from the partial reduction and phase instability of BYC5 at the oxygen-lean side; no degradation of the conductivity of BYC5 was observed over a week-long period in an oxidizing atmosphere.[10] In contrast, the (SSC + Pd), (LSGM + Pd), and (YSZ + Pd) composites all showed a stable oxygen permeation flux under the conditions of our measurements. Unlike the ac impedance measurement made on solid electrolytes, the oxygen permeation measurement contains, in addition to the bulk transport, a contribution from the surface exchange reaction that cannot be so easily resolved. The LSGM electrolyte has a higher bulk oxide-ion conductivity than SSC. Therefore, a slightly higher Jo_2 in the (SSC + Pd) than in the (LSGM + Pd) is probably due to a lower surface-exchange activation energy where the interface triple-phase boundary length is smaller, see Fig. 3b. On the oxygen-lean side, a lower oxygen partial pressure increases the mixed conductivity of SSC,
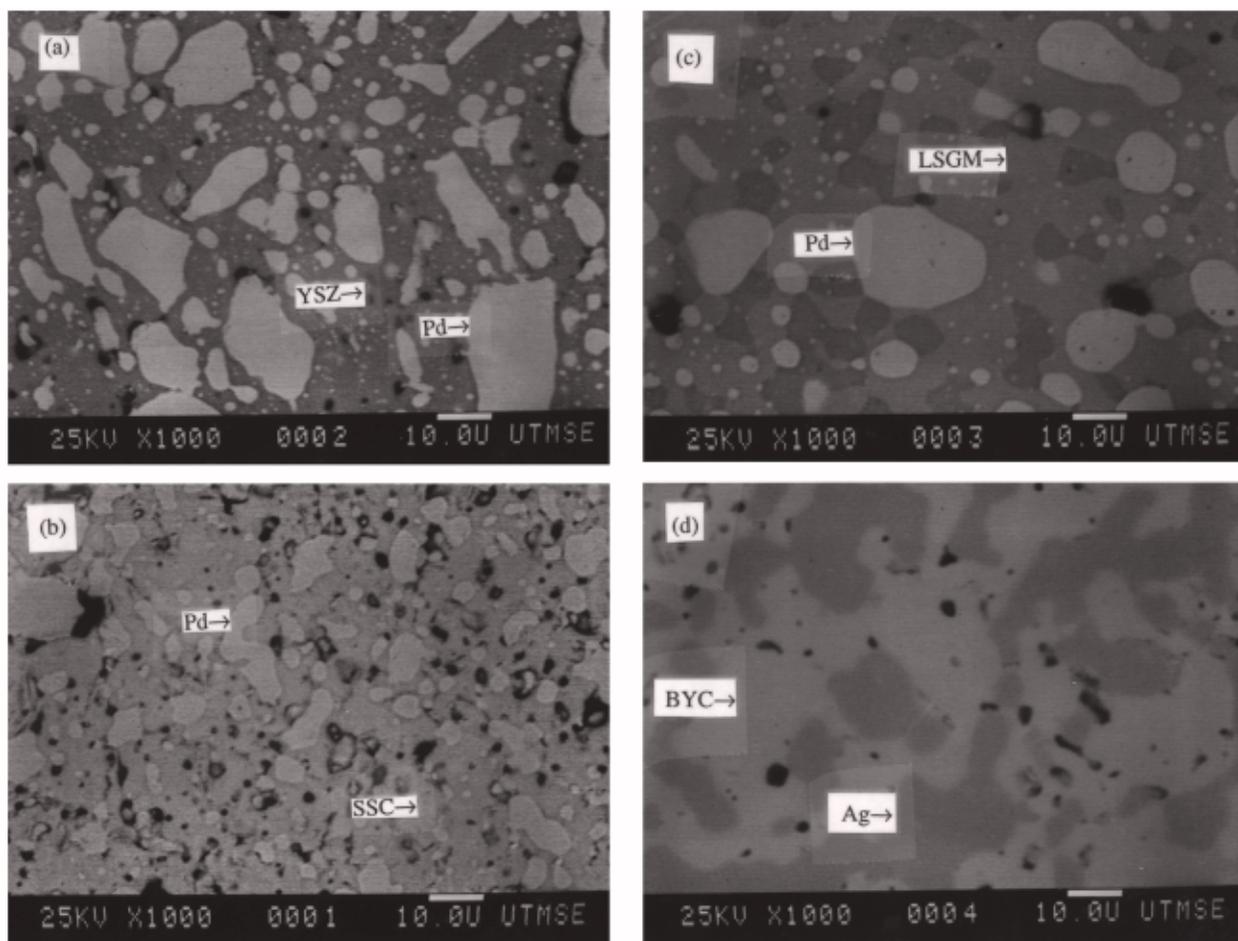
Figure 3. Microstructures of the prepared oxide-metal composites (a) (YSZ + Pd), (b) (SSC + Pd), (c) (LSGM + Pd), and (d) BYC5+Pd.
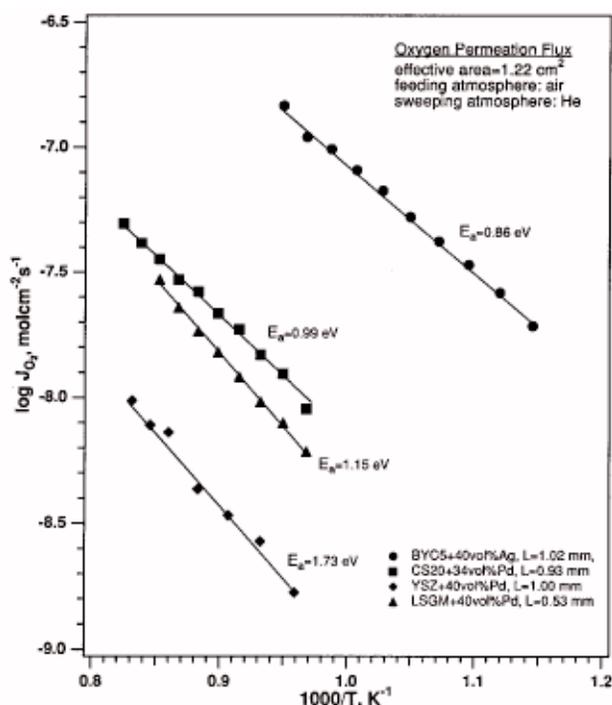

Figure 4. Comparisons of oxygen permeation flux among the studied composites.

which contributes to the electron percolation pathway increases the surface exchange rate. Considering that even a lower oxygen partial pressure would be encountered with CH_4 plus syngas and in other practical applications, an enhanced mixed conductivity of SSC could reduce the amount of costly Pd needed to obtain an electronic percolating pathway. Therefore the (SSC + Pd) composite appears to be the most promising candidate for oxygen separation, offering a relatively high Jo_2 and lower costs. It is worth mentioning that Fig. 4 represents Arrhenius plots for different composite mixed conductors under a fixed flow rate instead of a fixed po_2 gradient. However, these plots indeed reflect the maximum values because the composite mixed conductors with lower Jo_2 are always exerted on a larger po_2 gradient under a given flow rate.

Theoretically, E_a of the oxygen permeation should be the same as that for oxide-ion conduction σ_O provided that σ_O is independent of po_2 and bulk diffusion dominates the permeation process. Practically, however, none of the composites behaved ideally. Comparison of Fig. 4 with the published activation energies for oxide-ion conduction in the pure oxides (E_a = 0.78 eV for BYC5 from 750 to 600°C,[10] 0.78 eV for SSC from 900 to 750°C,[13] 0.82 eV for LSGM from 800 to 750°C[14] and 0.87 eV for YSZ from 1300 to 700°C[15]) shows that the activation energy of the permeation flux for each composite is higher. The (BYC5 + Ag) has the nearest values because of its fast surface oxygen exchange[16] and well-connected network. Presumably, a slow surface oxygen exchange due to insufficient electron supply and/or generation caused by a poorly connected metallic phase would take control of the overall permeation process in the other composites, which increases their activation energies. This question can be determined by measurements made for several po_2 gradients. It is also found from our measurements
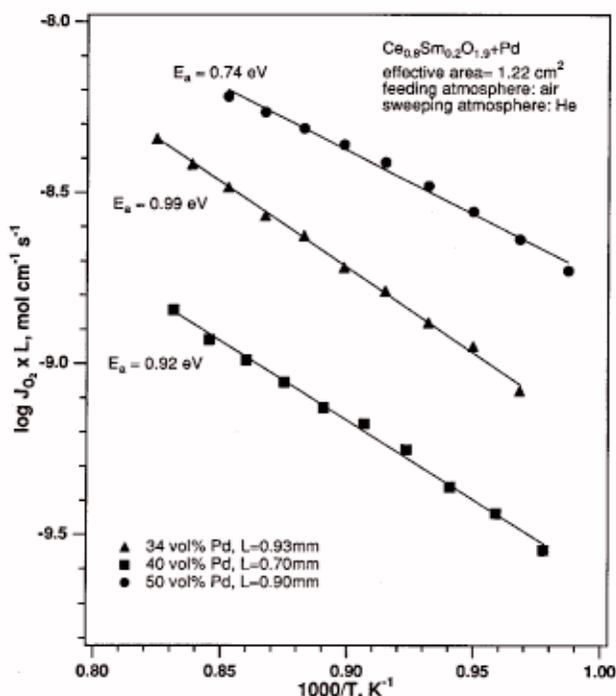
Figure 5. Effect of Pd content on the oxygen permeation rates normalized to the thickness L of the (SSC + Pd) composite.

that thinner samples always give lower activation energies, which signals control of the oxygen permeation by the rate of surface oxygen exchange. Optimization of the microstructure of a composite mixed conductor, especially the metallic phase, seems to be a key factor in minimizing the activation energy.

Effect of Pd content on the oxygen permeation rate.—Figure 5 shows the effect of Pd content on the oxygen permeation rates normalized to the thickness L of the (SSC + Pd) composite; the surface reaction is incorporated into the permeation process. A maximum Jo_2 at 40 vol % Pd indicates a percolation threshold concentration for the electronic pathway. It is expected that the percolation threshold concentration would be lower if a well-defined network had been obtained and a CH_4 atmosphere had been used. Based on this result, the Pd content was fixed at 40 vol % for all the other composites investigated in this study.

Conclusions

XRD shows that under the given preparation conditions, no reactions take place between the oxides and the metals in the investigated composites (BYC5 + Ag), (SSC + Pd), (LSGM + Pd), and (YSZ + Pd). Microstructural examination revealed significant morphological differences in the composites. These differences correlate with higher activation energies for the permeation process in the composites compared to electrical conduction obtained by ac impedance analysis in the pure oxides, which indicates possible surface reaction control over bulk diffusion in the permeation measurements. Even though (BYC5 + Ag) yields the highest Jo_2 among the tested composites, its instability at lower oxygen partial pressure prohibits its use for the conversion of CH_4 to syngas. The (SSC + Pd) composite appears to be a promising composite for oxygen separation because of the mixed conductivity of the oxide at low po_2, but the morphology of the composite must be optimized. It is predicted that use of CH_4 in a practical reactor would lower the percolation threshold concentration of Pd needed for electronic percolation in a (SSC + Pd) composite, which would reduce the cost of practical oxidation; but partial oxidation on the surface of an oxide must compete with total oxidation.

Acknowledgments

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