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Glow-discharge enhanced permeation of oxygen through silver

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The permeation of oxygen through Ag_{0.05}Zr over the temperature range of 300–650 °C under glow-discharge conditions has been studied and compared to the permeation of thermally dissociated molecular oxygen. A low-energy dc glow-discharge in O₂ has been employed which produced approximately 10% atoms. The permeation rate during the glow discharge was found to be much higher (a factor of ~10) than without the glow discharge. The small fraction of oxygen atoms generated appears to dominate the permeation because of much higher solution probabilities. Below 500 °C, the activation energy for the permeation with glow discharge was found to be 15.5 kcal/mol compared to 22.0 kcal/mol without glow discharge (molecular oxygen). Above 500 °C, the enhanced permeation with glow discharge gradually diminishes with increasing temperature and approaches that observed without the glow discharge at high temperature; the reason for this is primarily because of the thermal instability of the supersaturated high-pressure interface where atoms recombine and desorb back into the gas phase.

I. INTRODUCTION

Silver is well known to be more permeable to oxygen than other materials.^{1–5} The transport of oxygen through Ag normally proceeds by a sequence of steps which include dissociative adsorption of molecular oxygen at the upstream surface, the dissolution of the atomic oxygen into the bulk, and the subsequent migration of the atoms between octahedral sites of the lattice (or through defects) until they arrive at the vacuum interface downstream where recombination to O₂ occurs with subsequent desorption to the gas phase. We have previously reported⁶ that dc glow discharge can generate a much higher flux through a silver membrane than normal thermal dissociative permeation, but have not examined the parametric variances. In order to understand more about the mechanism of the increased flux, we have conducted similar experiments using a Ag_{0.05}Zr membrane over the temperature range of 300–650 °C, and specifically examined the transport as a function of a number of parametric changes. The addition of a small amount of Zr was intended to increase the oxygen sticking coefficient and the oxygen surface concentration.

II. EXPERIMENT

Figure 1 schematically shows the upstream (supply) and downstream (detection) regions of the cell separated by the membrane. Since oxygen atoms naturally tend to recombine or react with other species, a concerted effort has been made to keep the glow region close to the membrane by using the membrane as one of the electrodes (anode). We have chosen the probe as the cathode to eliminate damage to the membrane surface caused by oxygen ion bombardment and to insure that the permeation occurs from ordinary oxygen atom and molecule adsorption. The

permeation apparatus used in this work includes a quadrupole mass spectrometer (QMS) and two ion gauges as the detection instruments and a Ag_{0.05}Zr membrane of 2.01 cm² area and 0.32 mm thickness, sealed between two stainless-steel miniflanges (3.38 cm diam). The small addition of Zr has been observed to increase the flux of oxygen slightly with almost a negligible change in diffusivity, presumably because of the increased sticking coefficient for the molecular oxygen.⁷ The system is primarily pumped in the downstream region by ion and sublimation pumps which develop an ultimate pressure of approximately 5×10^{-11} Torr. The upstream region is pumped by ion and molecular drag pumps which develop an ultimate pressure of approximately 2×10^{-9} Torr. The O₂ gas used was research grade pure (99.995) and cleaned of condensables by cold trapping. The integrity of the gas species was checked by an analytical mass spectrometer and by the system QMS after admission to the upstream side. Details of this system have been described previously.⁵

The steady-state flux (J_{eq}) through the membrane can be determined from the pressure difference $P_{\text{eq}} - P_p \approx P_{\text{eq}}$ between the downstream detecting volume (P_{eq}) and the main pump (P_p) by the relation:

$$J_{\text{eq}} = \frac{P_{\text{eq}} f}{AkT}, \quad (1)$$

where k is Boltzmann's constant, T is the gas temperature, and A is the membrane area.

The diffusivity data for the permeation of planar membranes is obtained in the manner described by Crank.⁸ The diffusivity D is assumed to be independent of concentration C , so that

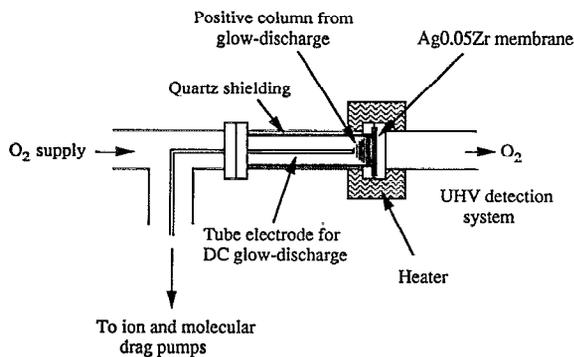


FIG. 1. Permeation cell showing O₂ supply side region (upstream), glow-discharge electrode, and the detection region (downstream).

$$\frac{\partial C}{\partial t}(x,t) = D \left(\frac{\partial^2 C(x,t)}{\partial x^2} \right). \quad (2)$$

The boundary conditions are

$$C(x,t=0) = g(x), \quad (3a)$$

$$C(x=0,t) = C_1, \quad (3b)$$

$$C(x=d,t) = C_2, \quad (3c)$$

where $g(x)$ is generally assumed to be a linear function and d is the membrane thickness.

The pressure-decay method has been used to determine the diffusivity in order to remove upstream surface effects. The diffusivity can then be calculated according to the equation

$$\frac{J(t)}{J_{eq}} = -2 \sum (-1)^n \exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right). \quad (4)$$

The first term is accurate to within 99% for the conditions used in this study so the diffusivity can be represented by

$$D = 0.30d^2\tau^{-1}, \quad (5)$$

where τ is the time in seconds for a pressure decay in the downstream region of one order of magnitude or $P(t)/P_{eq} = 0.1$.

III. RESULTS AND DISCUSSION

Figure 2 shows the permeation rate of oxygen through the Ag_{0.05}Zr membrane at an upstream pressure of 3.0 Torr and a membrane temperature of 450 °C. At steady state, the characteristic O₂ flux with thermal dissociative adsorption is about $3.4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Application of 350 V (dc), which was required for this geometry and pressure, and 35 mA glow discharge rapidly increased the downstream O₂ flux to $2.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. Upon termination of the discharge power, the signal returned to the original steady-state permeation level consistent with thermal dissociative adsorption. The main formation process of atomic oxygen in the glow-discharge is the excitation of the Herzberg ($A^3\Sigma^+$) and the Schuman–Runge ($B^3\Sigma^-$) system by electron impact leading to dissociation:

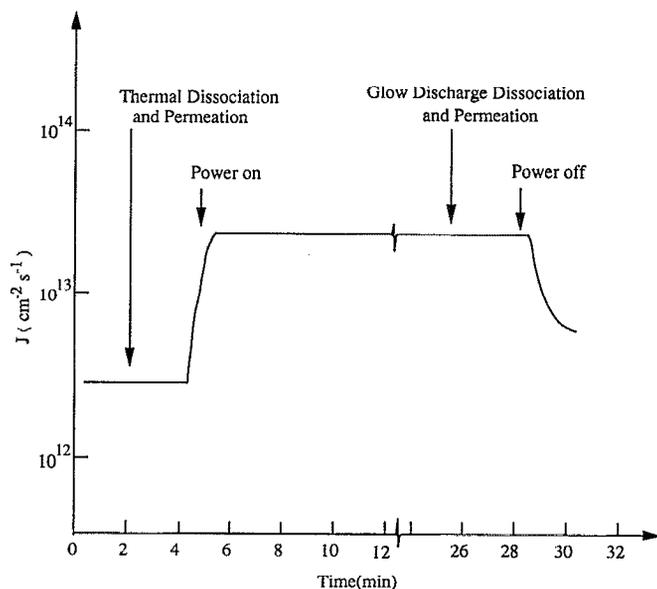
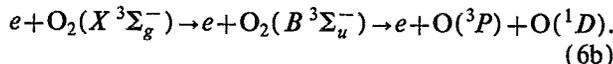
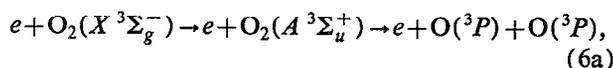


FIG. 2. Downstream flux variations due to oxygen permeation with and without upstream glow discharge.



The dissociation rate increases with the current due to the increasing electron concentration. Sabadil and Pfau⁹ compared the dissociation rate in the middle part of the positive column (Wrede–Hartek method) to the values at the inlet of the U tube (O₃ method) and found a uniform axial distribution of the O atoms. They concluded that the diffusion of O atoms is sufficiently fast to eliminate axial concentration gradients due to the axial gas flow in the positive column. According to this method, the dissociation rate in this work will be about 0.06 with 10 mA discharge and 0.11 with 35 mA discharge. Since the positive column in this work is very close to the silver membrane (anode), we assume a uniform atomic oxygen density in the vicinity of the silver membrane. The increased signal during the glow discharge suggests that the solution probability for atomic oxygen (and therefore the surface concentration) is substantially greater than that for ordinary permeation where only O₂ molecules are dissociatively adsorbed onto the surface without glow discharge.

Figure 3 shows that the permeation rate varies linearly with glow-discharge current. Basically, when the current (primarily electrons) was increased, the dissociation of O₂ increased proportionately, thus resulting in a proportional increase in the O atom partial pressure. The reversibility of this process, i.e., the decrease in the downstream flux with a reduction in discharge current, was also established. This is consistent with the work of Sabadil and Pfau who also observed a linear increase in oxygen atoms with discharge current.⁹ They measured the atom densities by two meth-

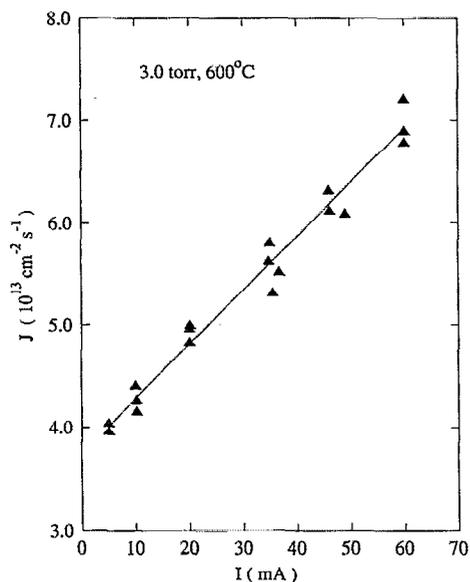


FIG. 3. Downstream flux as a function of glow-discharge current at 3.0 Torr upstream pressure and 600 °C membrane temperature.

ods (the ozone method and the Wrede-Harteck method) and the results are in a good agreement with each other. At 600 °C, with the geometry shown in Fig. 1, the flux increases $5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for each mA of discharge current. Since the Ag membrane was the anode, no ion bombardment effects, such as surface modification and/or surface sputtering occurred. Although electron bombardment of the anode may have generated some loss of oxygen at the surface, the desorption cross section for this process is quite small ($\sigma < 10^{-18} \text{ cm}^{-2}$). Furthermore, this process would work to decrease the downstream flux with increasing discharge current. It therefore appears that the increase in flux is due to an increase in the surface concentration of oxygen at the high-pressure interface. The distribution of dissociated atoms is, however, a strong function of the cathode probe distance from the membrane (see Fig. 4). For this geometry and discharge current, 4–5 mm appears to be the position to maximize the atomic oxygen density in the vicinity of the membrane and therefore maximize the surface incidence rate.

Clearly, the glow discharge should have no effect on the diffusivity since that is a bulk property independent of the gas phase. Figure 5 shows the diffusivity (D) measured at 3.0 Torr with and without glow discharge and at 100 Torr without glow discharge. The Arrhenius plot reveals two distinctly linear regions. The break in the diffusivity at about 630 °C has been observed previously and has been attributed to the higher efficiency of traps at low temperatures. There is no variation in the diffusivity for these conditions, although enhanced diffusion of hydrogen in molybdenum has been reported in glow discharge.¹⁰ An atom will lose all of its gas phase energy when it is adsorbed and dissolved into the bulk. At this point, it becomes thermalized and its diffusion is random walk controlled by the temperature and the activation barrier

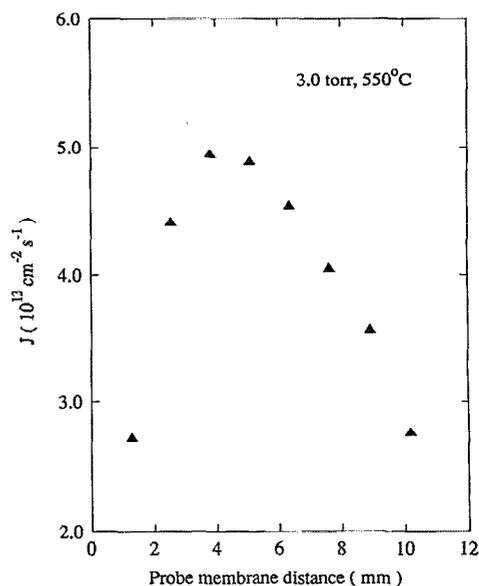


FIG. 4. Variation in the flux as a function of cathode to anode (membrane) distance.

between sites. Since the diffusion in the bulk is much slower than the adsorption and desorption steps, it is generally rate controlling. Assuming that bulk diffusion obeys Fick's law, it is clear that the significant increase in the downstream flux with glow discharge is primarily due to the increasing oxygen concentration on the upstream surface, which, in turn, increases the concentration gradient through the membrane thickness. This situation is schematically illustrated in Fig. 6. A comparison of the activation barrier for diffusion in this work to that of the previous studies of oxygen in pure Ag is interesting. Our earlier work⁵ with pure Ag ($\Delta H_D = 11.05 \text{ kcal/mole}$) compares

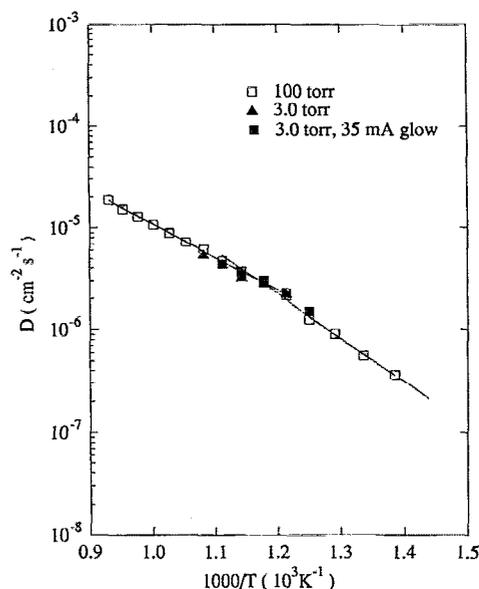


FIG. 5. Diffusivity as a function of reciprocal temperature with and without supply side glow-discharge-assisted dissociation.

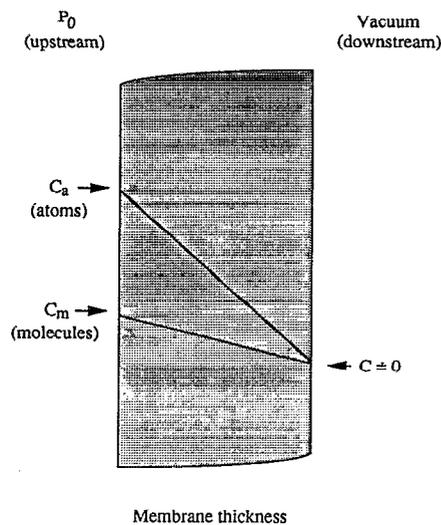


FIG. 6. The concentration profile of the oxygen in the membrane is presumed to be much greater with glow-discharge-assisted dissociation because $C_a > C_m$.

favorably with the work of Eichenauer and Mueller¹ and Ramanarayanan and Rapp² who determined values of ΔH_D to be 11 and 11.6 kcal/mol, respectively. In this work, our value of $\Delta H_D = 13.5$ kcal/mol in the high-temperature regime ($T > 600^\circ\text{C}$) is somewhat greater because of the addition of the Zr providing a slightly distorted lattice and a more chemically reactive element toward oxygen. The impact of the 0.05 wt % Zr is even more significant at low temperature, $T < 600^\circ\text{C}$, where the value of $\Delta H_D = 20.1$ kcal/mol. The details of the effect of Zr on the O transport are discussed elsewhere.⁷

Figure 7 shows an Arrhenius plot of the oxygen per-

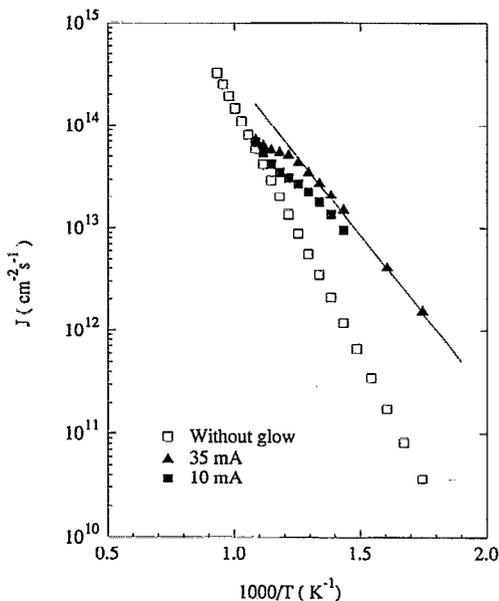


FIG. 7. Downstream flux as a function of reciprocal temperature. The break in linearity for the permeation with glow discharge occurs at 500°C and approaches the value without glow discharge at about 650°C .

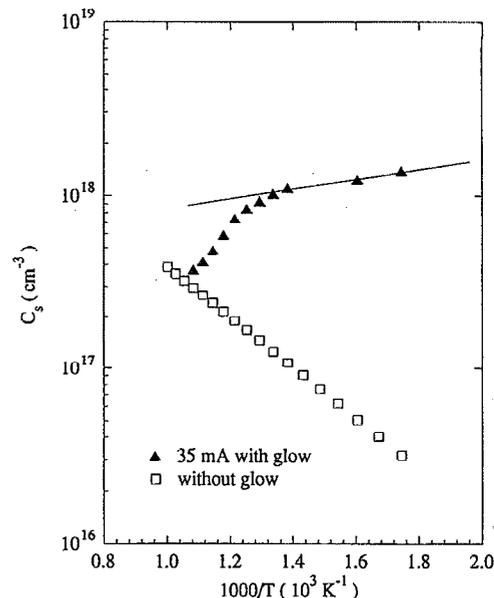


FIG. 8. The upstream concentration variation as a function of reciprocal temperature with and without glow discharge.

meation flux (J_{gd}) at a 3 Torr upstream pressure with 10 and 35 mA glow-discharge conditions. Also shown is the permeation flux (J_m) with the same upstream pressure but without glow discharge. The phenomenon of the flux increasing with the initiation of the glow discharge is most pronounced at lower temperatures (below 550°C). Up to 500°C , the glow-discharge enhanced permeation rate is the expected exponential function of temperature. The activation energy for this process, $\Delta H_J = 15.5$ kcal/mol (since the glow-discharge precludes equilibrium, we report ΔH_J instead of ΔH_K), is lower than that for ordinary thermal dissociative permeation, $\Delta H_K = 22.0$ kcal/mol. Since the permeation process includes the adsorption and dissolution steps, this is consistent with a higher solution probability with a corresponding lower activation energy because of the glow discharge. For temperatures above 500°C , however, the permeation curve departs from linearity, with the magnitude of J_{gd} gradually approaching that of J_m . This is very similar behavior to that observed in the permeation of atomic hydrogen through molybdenum¹⁰ and quite likely represents atom recombination and desorption back into the gas phase at higher temperatures. This has been observed previously in oxygen charged (permeated) Ag membranes when they were heated above 630°C .⁵

Assuming that bulk diffusion obeys Fick's first law and assuming that the downstream surface concentration is zero, the upstream surface concentration can be determined from

$$C_s = \frac{dJ_{eq}}{D} \quad (7)$$

Figure 8 shows that the upstream surface concentration, C_s , varies with reciprocal temperature, with or without glow discharge. These curves are taken from the data in Figs. 5 and 7. The concentration from thermal dissociative

adsorption and dissolution for the case without glow discharge, varies linearly in an Arrhenius plot as expected, but this is not true for the glow-discharge case. At lower temperatures, $T < 500^\circ\text{C}$, C_s weakly decreases with increasing temperatures. The magnitude, however, is substantially greater than that for molecular oxygen without glow discharge. At 500°C , for example, C_s with glow discharge is 9.31×10^{17} which is 6.4 times larger than the value of C_s without glow discharge (1.45×10^{17}). At 400°C , the factor is 16 times greater. This clearly indicates that the oxygen atoms result in an oxygen solid solution at the high-pressure interface that is supersaturated with respect to that for the molecular oxygen. The weak, positive slope, temperature dependence of C_s at low temperatures with glow discharge further confirms the supersaturated surface conditions. The positive slope is a clear departure from Sievert's law which, of course, is for equilibrium conditions. This is not surprising, however, since the glow-discharge conditions are nonequilibrium and produce concentrations well above the solubility value determined from Sievert's law. At temperatures above 500°C , C_s decreases with increasing temperature, probably because of the aforementioned increasing desorption rate. Ultimately, at temperatures approaching 700°C , the total flux finally approaches the case without glow discharge, i.e., ordinary dissociative permeation.

IV. SUMMARY

The permeation of atomic oxygen generated by a dc glow discharge through a Ag0.05Zr membrane over the temperature range of $300\text{--}650^\circ\text{C}$ has been studied and compared to the ordinary permeation of molecular oxygen. The following observations are presented:

(1) At low temperatures ($T < 500^\circ\text{C}$), under glow-discharge conditions, the surface concentration of oxygen atoms is above the solubility limit for ordinary thermal dissociative permeation.

(2) At low temperatures ($T < 500^\circ\text{C}$), the flux under glow-discharge conditions is much higher than the flux without glow discharge, because the concentration gradient is substantially higher due to the higher solution probability for atomic oxygen. The activation energy for this process is 15.5 kcal/mol compared to the activation energy without glow discharge which is 22.0 kcal/mol.

(3) At temperatures above 500°C , the permeation with glow discharge gradually approaches the same magnitude as the permeation without glow discharge because of the instability of the supersaturated state and its ultimate decay toward equilibrium.

(4) At a constant temperature, the permeation flux increases proportionally to the discharge current thus indicating a proportional increase of oxygen atoms in gas phase.

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