Oxygen permeability in $La_2NiO_{4+\delta}$

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Mixed oxygen ion and electron conductors, like $La_2NiO_{4+\delta}$, may find use as oxygen permeable membranes for oxygen production and direct partial oxidation of hydrocarbons. This study aims at a better understanding of the surface kinetics involved during oxygen permeation through $La_2NiO_{4+\delta}$.

Several authors have reported the oxygen permeability and transport properties of $La_2NiO_{4+\delta}$. The material has the perovskite related K_2NiF_4 structure, and contains excess oxygen in interstitial positions.(1) Vashook et al. measured the oxygen nonstochiometry of $La_2NiO_{4+\delta}$, and the oxygen flux of both undoped and strontium doped samples. The highest permeability was found for the undoped sample.(2) Skinner et al. measured the oxygen tracer diffusion coefficient and the oxygen surface exchange coefficient by SIMS.(3) No systematic investigation of the permeability as a function of sample thickness has been found.

In the present work, we report on oxygen permeability of sintered, dense disks of $La_2NiO_{4+\delta}$. The samples are characterised by SEM and XRD. The steady state oxygen permeability is measured at different temperatures and oxygen gradients, using mass spectrometry analysis. A series of 5 membranes of different thickness is investigated to evaluate the degree of surface control.

The material is synthesised by a wet chemical route, using citric acid as a complexing agent. Upon dehydration and annealing at 1000ºC, single phase $La_2NiO_{4+\delta}$ is obtained. Sintering at 1350°C provides dense samples. During the measurements, feeding a mixture of oxygen and nitrogen to one side of the membrane, and a mixture of helium and oxygen to the other side creates the oxygen gradients, and allows determination of the leakages.

Figure 1 shows the Arrhenius plot of the flux of a 0.5 mm thick membrane. The oxygen gradient was established by feeding oxygen or air to the primary side and helium with oxygen partial pressure 0.001 atm to the secondary side. The material has a high permeability of oxygen. At 1000°C the flux was 6.3 mmol $m^{-2}s^{-1}$.

To investigate the degree of surface control, 5 different samples, ranging from 0.3 to 2.5 mm thickness, were investigated at temperatures between 850°C and 1000°C. Figure 2 shows the oxygen flux versus inverse membrane thickness. The oxygen flux of the thin samples showed almost pure surface control, whereas the flux of the thick samples showed mainly bulk influence. The characteristic thickness of the membrane is consequently found in this range. A more detailed analysis of the data in terms of characteristic sample thickness and dependencies of gradient and temperature will reported in the full paper.

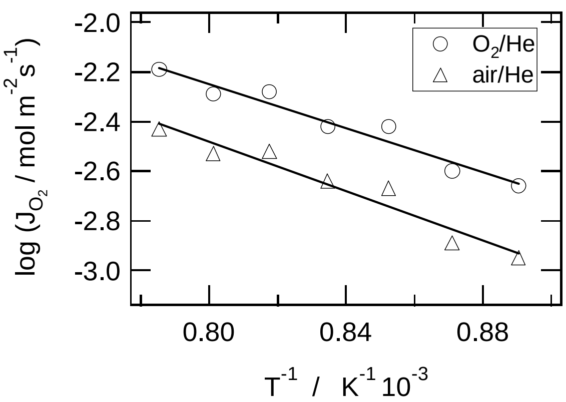

Figure 1: Arrhenius plot of the flux of a 0.5 mm thick membrane. The two sides of the membrane are fed pure oxygen or air and helium with oxygen partial pressure 0.001 atm.

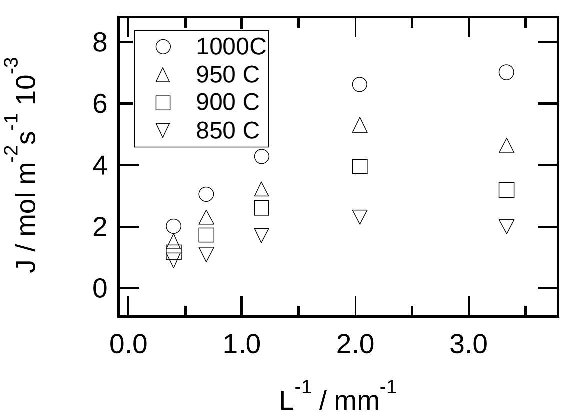

Figure 2: The oxygen flux versus inverse sample thickness. The two sides of the membrane are fed pure oxygen and helium with oxygen partial pressure 0.001 atm.

1. J.D. Jorgensen, B. Dabrowski, S. Pei, D.R. Richards and D.G. Hinks, Phys Rev B **40**, 2187 (1989)
2. V.V. Vashook, I.I Yushkevich, L.V. Makhnach, S.P. Tolochko, I.F. Kononyuk, H. Ullmann and H. Altenburg, Solid State Ionics **119**, 23 (1999)
3. S.J. Skinner and J.A. Kilner, Solid State Ionics **135**, 709 (2000).