BIMEVOX ADAPTABILITY IN OXYGEN GENERATOR DEVICE

[a]C.Pirovano, [a]R.N. Vannier, [a]E. Capoen, [a]G. Nowogrocki, [b]M. Anne, [a]J.C. Boivin and [a]G. Mairesse

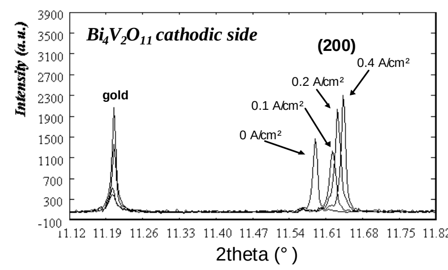
[a]Laboratoire de Cristallochimie et Physicochimie du Solide, ENSCL, B.P. 108, 59652 Villeneuve d'Ascq Cedex, France

[b]Laboratoire de Cristallographie, UPR 5031, 25 Avenue des Martyrs, B.P. 166, 38042 Grenoble Cedex 09, France

email: vannier@ensc-lille.fr

Electrochemical separation of oxygen from air, using a solid oxide electrolyte, is a very attractive approach for the small scale production of oxygen with a high purity (100%). Domains such as aerospace, medicine and electronic are interested in, since it allows the in-situ production of a highly pure oxygen with a given flow, without any constrain of stock.
The principle of these Ceramic Oxygen Generators relies on the ability of oxide to migrate through ceramics at elevated temperature. Basically, there are two concepts of such devices: the current driven membrane and the pressure driven membrane. In the first case, the membrane is a pure oxide ion conductor, in the second it is a mixed, electronic and oxide, one.
In the case of the current driven membrane, a current, from an external circuit, is applied at the cathode where oxygen is dissociated according to the following reaction: $O_2 + 4\ e^- \rightarrow 2O^{2-}$. Then, oxides migrate through the ceramic and recombine in oxygen at the anode according to the reverse reaction. The advantages of such a device are numerous: it allows a precise control of the oxygen flow, and can work in compression. Moreover, the process is completely reversible and the generator can be an extractor.
In the second case, because the membrane is a mixed conductor, no external current circuit is needed. The motor is the oxygen partial pressure gradient between the two surfaces of the membrane.
The main disadvantage of the current driven membrane generator is it needs almost three components: a cathode, an anode and an electrolyte, generally three different materials that must be physically and chemically compatible, with close thermal expansion coefficients and no chemical reaction.
Indeed, the oxygen transfer at the surface of pure oxide ion conductors is usually very bad, therefore electrodes are necessary and the transfer occurs at the three phase boundary, gas-electrode-electrolyte where oxygen molecules, oxides and electrons gather.
However, in the mid eighties, B.C.H. Steele [1] et al. showed evidence that Bi^{III} could have a catalytic effect on the oxygen dissociation. In the same time, M. Dumélié et al [2] built a membrane with a bismuth-based phase as electrolyte, co-pressed between two gold grids, without any other electrodes. They obtained an oxygen rate of about $1cm^3.cm^2mm^{-1}$ at 600°C.

Bismuth-based materials are very good oxide conductors and among these bismuth-based materials, the BIMEVOX exhibit the highest conductivity at moderate temperature (≤600°C). A conductivity value of $10^{-3}S.cm^{-1}$ was observed for the BICUVOX.10 at 300ºC. These phases derive from the parent compound $Bi_4V_2O_{11}$ by partial substitution for vanadium with another metal. For instance, BICUVOX.10 is obtained by the partial substitution for vanadium with 10% copper, giving the following composition: $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$. These materials are mainly pure oxide ion conductors, however at temperature >500°C and at high oxygen partial pressures, an increase of the conductivity was observed for the BICOVOX phases, indicating a p-type electronic contribution to the conductivity. In contrast, for BICUVOX, an increase of the conductivity was noticed at low oxygen partial pressures, corresponding to a n-type electronic contribution.
Because of this small electronic contribution, these materials could not be used as oxygen sensor but remain good candidates as electrolyte in Ceramic Oxygen Generator.
Simple membranes, made of co-pressed BIMEVOX pellets in between two gold grids were tested. A faradic efficiency of about 100% was generally obtained for current density up to $1A/cm^2$, corresponding to an oxygen rate of $3.5cm^3/min/cm^2$ [3].
To follow the behavior of the membrane under current density, an in-situ X-ray diffraction experiment was performed under bias. Three compositions were selected: a BICUVOX, a BICOVOX and a slightly bismuth enriched $Bi_4V_2O_{11}$. Both cathodic and anodic sides were checked using synchrotron radiation.



In situ X-ray diffraction at 620°C for various current densities at the cathode of a $Bi_4V_2O_{11}$ membrane

The highest transformations were observed on the non - doped material, on cathodic side. Comparison with results obtained by chemical reduction under nitrogen and hydrogen atmospheres allowed us to confirm that, in this case, these modifications were due to a small reduction of the BIMEVOX material. When turning off the current, the initial phase was completely recovered, indicating the complete reversibility of the process.
This reversible transformation was rapid and confirmed the great adaptability of bismuth-based materials to act as electrode under significant current densities.
These results should lead to a considerable simplification of the design of BIMEVOX membranes for oxygen separation from air

ACKNOWLEDGEMENT
The authors are grateful to Dr Eric Dorehee for his help during the synchrotron experiment. The ESRF is thanked for providing synchrotron radiation facilities.

REFERENCES
[1] B.C.H. Steele, J.A. Kilner, P.F. Dennis, A.E. McHale, M. Van Hemert, A.J. Burgraaf, Solid State Ionics **18-19** (1986) 1038-1044.
[2] M. Dumélié, G. Nowogrocki, J.C. Boivin, Solid State Ionics **28-30**(1988) 524-528
[3] J.C. Boivin, C. Pirovano, G. Nowogrocki, G. Mairesse, P. Labrune, G. Lagrange, Solid State Ionics **113-115** (1998) 639-651