



	<b>Experiment title:</b> In situ dynamical electrolyte $\leftrightarrow$ electrode transformation of BIMEVOX membranes (ME=Cu, Co) under current density up to 1A/cm <sup>2</sup> at 900K	<b>Experiment number:</b> CH-506
<b>Beamline:</b> BM 16	<b>Date of experiment:</b> from: 26/11/98 to: 1/12/98	<b>Date of report:</b> 15/02/99
<b>Shifts:</b> <u>12</u> <sup>(*)</sup> /15	<b>Local contact(s):</b> Eric Dooryhee	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Michel ANNE*	Laboratoire de Cristallographie - CNRS-BP 166 38042 Grenoble Cedex 9
Jean-Claude BOIVIN*	Laboratoire de Cristalochimie et Physicochimie du Solide, ENSCL, BP 108 59652 Villeneuve d'Ascq Cedex
Gaëtan MAIRESSE*	" "
Guy NOWOGROCKI*	" "
Caroline PIROVANO*	" "
Pierre STROBEL*	Laboratoire de Cristallographie
Rose-Noëlle VANNIER*	Laboratoire de Cristalochimie et Physicochimie du Solide

Electrochemical oxygen separation from air using a ceramic oxide membrane is an important economical challenge. Such membranes can be involved in many industrial oxidation process, medical applications, catalysis and so on...

These ceramic oxide membranes are based on the redox reaction  $O_2 + 4e^- \xrightarrow{\frac{1}{2}} 2O^{2-}$  occurring at the cathodic side (1) and the anodic one (2), the  $O^{2-}$  anion migrating through the electrolyte. In a classical device such membranes are built up from a ceramic oxide exhibiting high oxide anion mobility, sandwiched between porous electrodes both associated with current collectors. The electrons flow exclusively through an external circuit connected to a power source. The weakness of such a device is the need for electrolyte and electrodes of different materials that can lead to chemical and mechanical incompatibility which can drastically affect its life durability.

Our materials designated as BIMEVOX exhibit properties which allow the electrolyte to locally act as electrodes (reversibly cathode or anode) under operating conditions [1]. These phases are mainly oxide anion conductors. They are obtained by partial substitution for vanadium in the parent compound  $Bi_4V_2O_{11}$  with a dopant. Depending on the nature of this dopant, a small n or p type electronic contribution to the conductivity is observed. A galvanic cell is obtained with a single phase BIMEVOX pelletized membrane (diameter about 10 mm, thickness about 3mm) with copressed gold grids on both sides as current collectors, connected to a galvanostatic power source.

The aim of this experiment was to follow the phenomena on both anode and cathode during oxygen pumping. To use the furnace available at the ESRF, a special support for the membrane was built in our laboratory.

<sup>(\*)</sup> On the 15 shifts allocated, only 12 shifts could be used due to technical problems on the heating device before our schedule experiments.

Due to the necessary time needed to optimise the assembly : furnace, support, the beam line calibration, and the lack of three shifts for technical reasons before our runs, only two samples have been tested :

- one of p type : a BICOVOX sample with composition  $\text{Bi}_2\text{V}_{0.87}(\text{Co}_{0.10}\text{Bi}_{0.03})\text{O}_{5.32}$ . Both anodic and cathodic sides have been tested under various current densities.
- one of n type : a BICUVOX.10 sample ( $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ ) for which only the anodic side has been checked.

The symmetry of these compounds is tetragonal. The evolution of unit cell parameters versus current density corresponding to the Cobalt compound is reported in Fig. 1. Gold parameter is also reported. It allows to determine the actual temperature on the membrane : the working temperature was about  $550^\circ\text{C}$ . However on anodic side, a small increase of the gold parameter when increasing the intensity is observed. It reveals a local thermal effect due to the exothermicity of oxygen releasing. It corresponds to an increase in temperature of  $50^\circ\text{C}$ . On cathodic side, this parameter remains quasi constant, that is consistent with the reduction process. The evolution of the a parameter of the ceramic is close to that of gold, while that of c parameter is more complicated. When applying about  $0.17\text{A}/\text{cm}^2$ , a sudden decrease of this parameter is observed, followed by an increase when increasing the current density. A reverse phenomenon is observed on cathodic side. In the case of BICUVOX.10 (Fig.2) only the anodic side has been tested. Conversely to the cobalt derivative, a small increase of c parameter is to be noticed when increasing the current density.

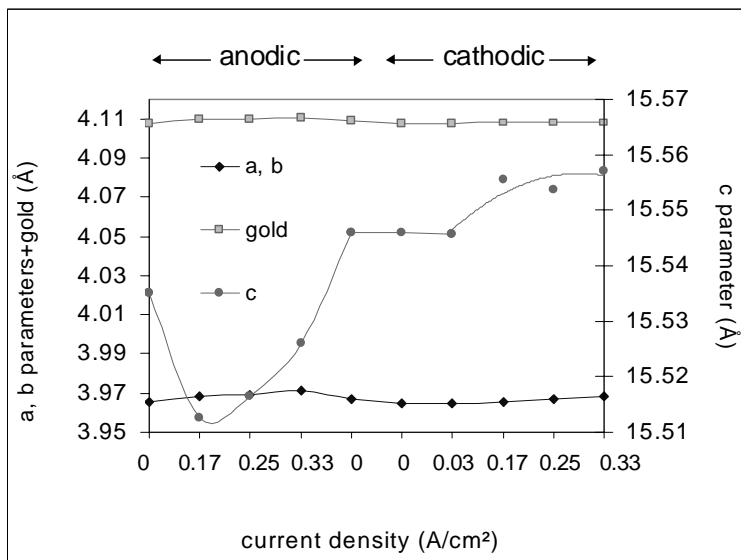


Fig.1  $\text{Bi}_2\text{V}_{0.87}(\text{Co}_{0.10}\text{Bi}_{0.03})\text{O}_{5.32}$   
unit cell parameters versus current density

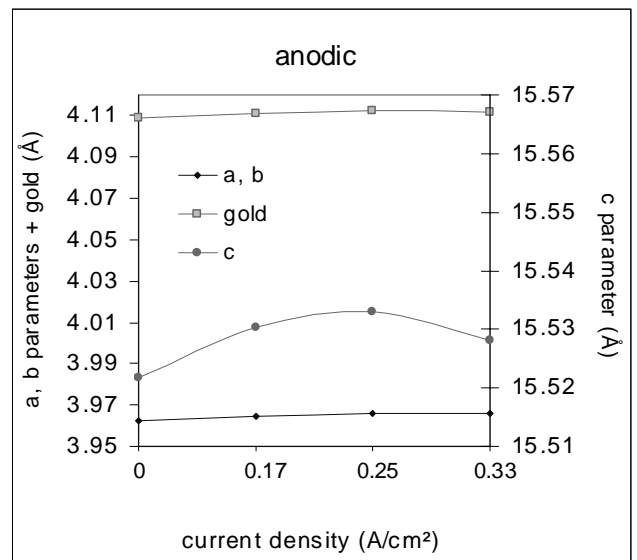


Fig.2 BICUVOX.10  
unit cell parameters versus current density

The difference in behaviour between the two different dopants can be explained by the different type of electronic conduction : n or p induced by the dopant. However it could also be due to the presence of bismuth in vanadium site for the cobalt phase, absent in the copper one. These experiments are just preliminary ones and have to be completed. The influence of bismuth in vanadium site and/or that of electronic conduction type have to be established. The reversibility of the cell has not been checked and is an important point for applications. However these results are very promising and due to the high resolution of BM16 may help us to understand the very complex but exceptional electric behaviour of these materials.

[1] J.C. Boivin, C. Pirovano, G. Nowogrocki, G. Mairesse, P. Labrune and G. Lagrange, *Solid State Ionics*, **113-115**, 639 (1998)