

Conductimetric Response linearity in γ' -Bi₂MoO₆

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Requisite conditions for electrical conductivity measurements in γ' -Bi₂MoO₆ are reviewed, to optimize its application as a conductimetric chemical sensor. Constant voltage DC electrical resistivity and AC complex impedance measurements demonstrate that: (1) ohmic behavior is limited to a 50 mV maximum voltage drop; (2) the influence of electrode polarization phenomena may be minimized by low frequency (10 Hz) AC measurements; (3) above 450°C, electrical conduction is dominated by intracrystalline conduction; (4) below this operating temperature, the influence of surface and electronic conduction inhibit sensitivity and selectivity; (5) low frequency AC measurements with 50 mV rms excitation reflect changes in the partial pressure of oxygen.

Keywords: Bismuth Molybdates; conductimetric chemical sensors; oxygen ionic conduction.

Se analizan las condiciones requeridas para las medidas de conductividad eléctrica en la fase γ' -Bi₂MoO₆, con el objeto de optimizar su aplicación como sensor químico conductimétrico. Medidas de resistividad eléctrica a potencial constante en c.c. y espectroscopía de impedancia en c.a., demuestran que: (1) el límite de comportamiento óhmico es 50 mV; (2) la influencia del fenómeno de polarización en los electrodos puede minimizarse mediante mediciones en c.a. a baja frecuencia (10 Hz); (3) por encima de 450°C la conductividad eléctrica está dominada por la componente intracristalina; (4) por debajo de esta temperatura, la influencia de la conducción electrónica y superficial inhiben la sensibilidad y la selectividad; (5) medidas en c.a., a baja frecuencia y excitación de 50 mV rms, reflejan cambios en la presión parcial de oxígeno.

Descriptores: Molibdatos de bismuto; sensores químicos conductimétricos; conducción iónica de oxígeno.

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1. Introduction

Although bismuth-molybdenum binary oxides, are solid electrolytes, capable of transporting ions via a defect mediated mechanism [1], the associated conductivity changes, in response to partial pressure of oxygen, have been deemed [2,3] insignificant. Sensitive responses are well known [4] for γ -Bi₂MoO₆, in alcohol and alkene bearing atmospheres, related to its catalytic properties [5] for selective oxidation reactions. The requisite experimental conditions for electrical conductivity measurements representative of oxygen stoichiometry changes are reviewed in this study, to optimize conductimetric sensing performance.

2. Experimental

9 mm × 3 mm cylindrical γ' -Bi₂MoO₆ pellets were prepared by solid state reaction of the component oxides, at 900°C in air. 100 nm thick circular gold electrodes were deposited by DC magnetron sputtering on both faces of the sample. A spring loaded ceramic fixture provided sample support and platinum contacts in pseudo four probe configuration, as well as thermometry with a Platinel II thermocouple, in an air tight cylindrical, 24 mm OD sillimanite reactor, placed in a Lind-

berg Minimate furnace. Controlled atmosphere was ensured by 100 cm³/min continuous flow of N₂-O₂ mixtures, with independent MKS 1179A mass flow controllers.

Potentiostatic DC I-V sweeps ranged from -1.000 to +1.000 V and AC measurements (50 mV rms, at 10 Hz) were undertaken with an EGG Signal Recovery DSP 7265 lock in amplifier, which resolved the real and imaginary current components, converted to voltage signals by a custom preamplifier (10⁴ V/A), with < 10⁻¹² A bias current. The thermal dependence of DC and AC conductivity (σ) was monitored in the cooling cycle, from 800°C to 250°C. Oxygen and ethanol partial pressure dependences of conductivity were analyzed at 500°C, with 50 mV rms and 10 Hz excitation.

3. Results and discussion

Current measurements, in response to applied DC voltage, in air, at 300°C and 500°C (Figs. 1a and 1b), demonstrate that, similarly to other ionic conductors, ohmic behavior is limited to a 50 mV maximum voltage drop.

Comparison of AC and DC conductivity (Fig. 2) clearly demonstrates the influence of electrode polarization phenomena, which are significantly reduced in low frequency (10Hz) AC measurements.

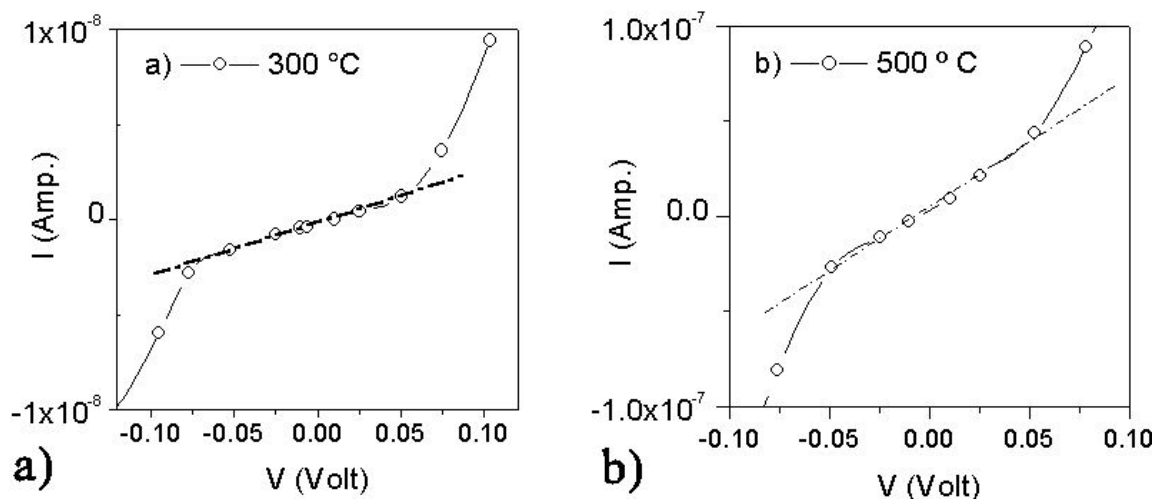


FIGURE 1. Potentiostatic dc I-V measurements in γ' -Bi₂MoO₆ at a) 300°C and b) 500°C.

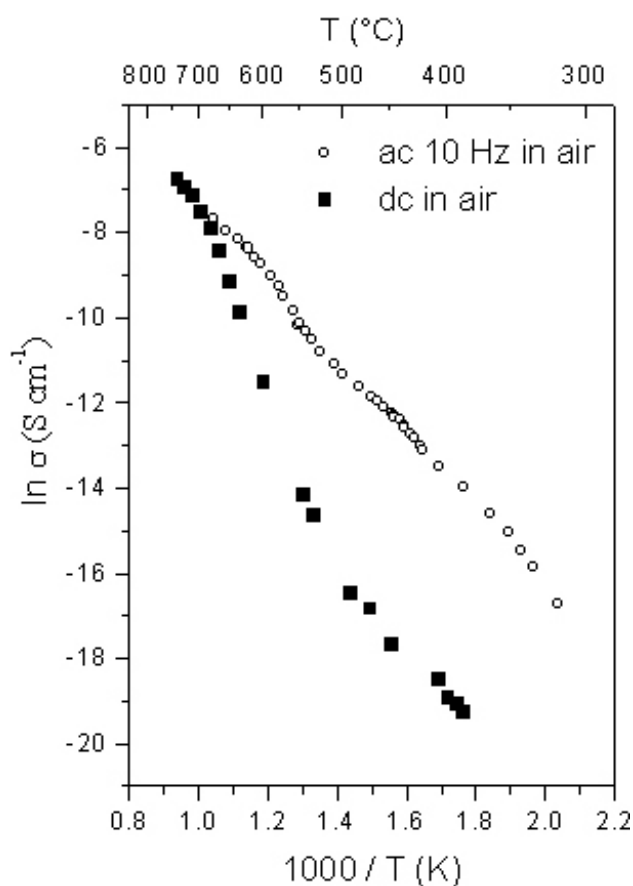


FIGURE 2. DC and AC temperature dependence conductivity of γ' -Bi₂MoO₆.

Above 450°C, electrical conduction is dominated by the intracrystalline component, which accounts for the robust response usually associated with these sensors. γ' -Bi₂MoO₆ is useful for conductimetric sensors [4] of reducing atmospheres, due to increased ionic conductivity proportioned to oxygen vacancy concentration. For instance, the conductivity change with a 1.3% by weight ethanol stimulus, at 500°C

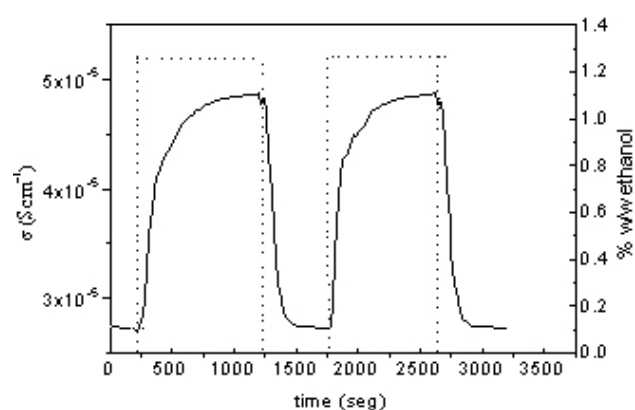


FIGURE 3. Electrical conductivity response in γ' -Bi₂MoO₆ to a 1.3 % w/w ethanol stimulus.

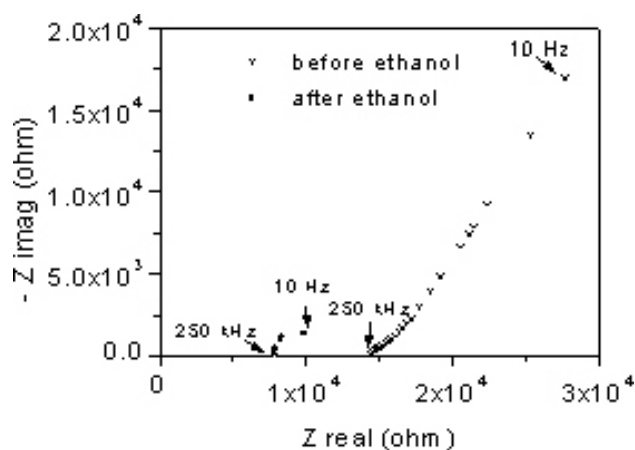


FIGURE 4. Impedance spectroscopy of γ' -Bi₂MoO₆, at 500°C, before and after exposure to 1.3 % w/w of an ethanol stimulus.

(Fig. 3), is quantitatively consistent with the 47% increase in ionic conductivity observed by impedance spectroscopy (Fig. 4). Below this operating temperature, the influence of surface and electronic conduction inhibits sensitivity and selectivity.

Below 500°C, the conductivity of γ' -Bi₂MoO₆ is increasingly dependent on the partial pressure of oxygen. Low frequency (10Hz) AC measurements with 50 mV rms excitation track changes of partial pressure of oxygen. At 500°C, a 43% conductivity (σ) increment can be observed (Fig. 5), when oxygen partial pressure is reduced from 1 atm to 0.32 atm. Response time to 80% of full deflection is 375 seconds, which is admittedly inadequate for control applications. Response times are limited by reactor dead volume and are currently under study.

Electrical conductivity dependence on oxygen partial pressure, would suggest alterations in metal-oxygen stoichiometry, implicit in oxygen vacancy concentration changes. However, impedance spectroscopy at various oxygen partial pressures (Fig. 6) suggests that such behavior is confined to the electrode-electrolyte interface, because the intracrystalline conductivity remains constant, which implies

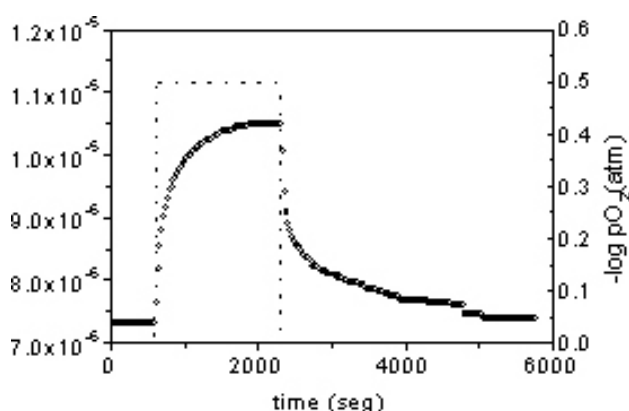


FIGURE 5. Electrical conductivity dependence with oxygen partial pressure.

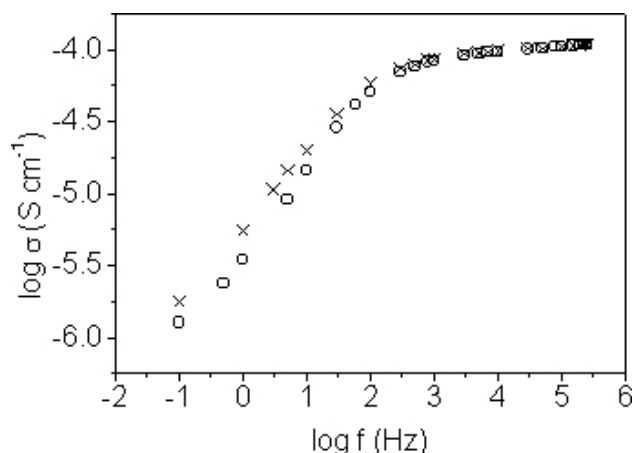


FIGURE 6. Logarithmic plot of γ' -Bi₂MoO₆ a.c. conductivity as a function of frequency, at 500°C, and $pO_2 = 1$ atm (o); $pO_2 = 0.32$ atm (x).

that some measure of electronic transport is present, consistently with the mixed character often attributed to this material [6–12].

4. Conclusions

In γ' -Bi₂MoO₆ conductimetric chemical sensors, ohmic behavior is limited to a maximum 50 mV excitation; electrode polarization can be reduced by AC operation. Oxygen ionic conduction, which dominates above 450°C, is responsible for the robust, reproducible sensor response to ethanol. Below 500°C electrical conductivity depends on oxygen partial pressure, which demonstrates that a mixed ionic electronic character cannot be excluded at low temperature.

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