



## Measuring ionic mobility in mixed-ionic-electronic-conducting nano-dimensioned thin films at near ambient temperatures

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### A B S T R A C T

Determining the ionic mobility in solids is often challenging due to inherently low ionic conductivities, typically requiring measurements at elevated temperatures, with high impedance analyzers and/or extended resistivity transients. Moreover, in many solids, the ionic conductivity is masked by dominant electronic conductivity, characterized by much higher carrier mobility.

By focusing our measurements on nano-dimensioned thin films, we are able to overcome such limitations. First, measurement time and temperature can be reduced, the latter to near ambient conditions, in selected materials, due to the considerably faster response of thin films compared to bulk materials to applied electrical stimulus. Second, the effect of the redistribution of ionic defects on the nano-scale, at relatively short time, has a major impact on the total conductivity.

The proposed method relies on measuring the nonlinear *I-V* response of thin films to linear voltage sweeps of high amplitude (relative to the thermal voltage) at different sweep rates. This differs from the impedance spectroscopy technique that analyzes the small signal response of systems. The method also differs from the well-known technique of cyclic voltammetry for deriving ion diffusion coefficients, as it does not require redox reactions to take place during voltage sweeps, thereby making it more generally applicable.

In this work, we present a novel and simple method for determining the ionic mobility from the measured *I-V* relations. It is determined from the position of a peak in the *I-V* relations and the sweep rate. The mobility so derived is compared with the one obtained by fitting the *I-V* relations based on solving the drift-diffusion equations for ions and electrons as published recently. Though the near ambient temperature ionic mobility was found to be seven orders of magnitude lower than the corresponding electronic one, it could nevertheless be well deconvoluted and characterized by both methods. The experimental results are compared with previous measurements on bulk and powder samples of molybdenum trioxide.

### 1. Introduction

Mixed-ionic-electronic-conductors (MIECs), as the term implies, conduct by both electronic and ionic mobile defects. MIECs are used in energy applications such as cathodes, and anodes in Solid Oxide Fuel Cells (SOFCs) [1], permeation membranes, [2] catalysts [3,4] and other novel types of devices [5]. There is now a growing trend in energy applications such as SOFCs, permeation membranes and catalysts to decrease operating temperature and to increase efficiency. Similar to trends for many decades in the microelectronics field, there is now also a growing trend towards miniaturization. All this requires new approaches for the characterization of MIEC materials, and in particular measuring ionic mobility, in thin films and at near to ambient temperatures. While methods for measuring electronic properties are well

established for a wide range of materials, from insulators to metals, there is a limited number of techniques for determining the ionic conductivity and the corresponding ionic mobility in MIECs.

The accurate measurement of ionic mobility in solids is challenging for several key reasons. Ionic motion, either by diffusion or drift, is a relatively slow process, being a thermally activated phenomenon, often characterized by high activation energies. At “reduced” temperature, less than 500 °C, long measurement times are necessary in order to detect the effects of ionic motion on properties. Recently, there has been a growing demand for applications where MIECs are operated at ‘reduced’ temperatures [1]. For example, memory devices based on memristive principles, that rely on MIECs, are designed to operate at room temperature. The characterization of their initial resistive state, including the ionic contribution, is essential for understanding the

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mechanisms that lead to electroforming and resistive switching in this new class of memory devices. Because ionic conductivity is typically a strongly activated process, its magnitude drops sharply with decreasing temperatures, making it very difficult to deconvolute from the much higher dominant electronic conductivity, particularly as one approaches ambient temperatures [6].

Isotopic exchange between  $^{18}\text{O}$  and  $^{16}\text{O}$  followed by secondary ion mass spectrometry (SIMS), can be used to extract very low values of oxygen ion tracer diffusivity [7,8]. The exchange process is usually performed at elevated temperatures due to limited rates of oxygen exchange between the  $^{18}\text{O}$  source and the oxide investigated. As a consequence, there are few reports and therefore little known about the ionic conductivity and mobility in MIECs near ambient temperature. Here we report on a novel method for measuring ionic mobility in MIECs. Low values of mobility can be well determined when the MIEC is in the form of a thin film. The method is based on measuring the  $I$ - $V$  relations in response to the application of a periodic triangular shaped voltage scan. At a given sweep rate and temperature, only one parameter must be extracted from the measured  $I$ - $V$  curve, the temporal position of a key peak, i.e. the time-to-peak as explained below. The mobility determined by this method from experimental data is compared with the mobility determined by fitting the previously reported solution of modeling of coupled ionic-electronic drift diffusion equations for this type of material [6,9]. The MIEC defect model assumes one single type of ionic defect (for example oxygen vacancy) compensated by one type of the electronic defect (e.g. conduction electron). Several examples of such materials are non-stoichiometric ceria  $\text{CeO}_{2-\delta}$ , titania  $\text{TiO}_{2-\delta}$  [10] and  $\text{MoO}_{3-\delta}$  [11] which upon reduction form doubly ionized oxygen vacancies,  $\text{V}_{\text{O}}^{\bullet\bullet}$ , that are compensated by the introduction of conduction band electrons,  $e'$ , resulting in n-type MIECs (Kröger-Vink notation is used to describe point defects). The dynamics of ionic defects in MIECs were found to have a major impact on the dominant electronic conductivity in MIECs [9,12]. Fitting theoretical  $I$ - $V$  curves to experimental data provides key information about systems' parameters, in particular, ionic mobility and its associated activation energy [6]. Yet the fitting is complex and we present below a considerably simpler method. A key strength of this new experimental method is that it derives the ionic mobility from the drift time of the ions and not from the slower diffusion time as in the aforementioned methods. Thus, applying voltages of high amplitude (relative to the thermal voltage) across nano-thin films results in significantly reduced measurement times and renders measurements at low temperatures (near to ambient) possible. No redox reaction or exchange of material with its surroundings is required or desired.

As mentioned above, while full modeling of MIECs allows one to extract the ionic mobility, it is a rather complex procedure [6]. By carefully examining our experimental results, we find a relation between the ionic mobility and a characteristic time, which we denote as time-to-peak ( $t_{\text{peak}}$ ) of the  $I$ - $V$  curve. A semi-empirical relation between the mobility, sweep rate and  $t_{\text{peak}}$  is derived starting from the drift time equation for the ions. Using the semi-empirical relation enables extracting an ionic mobility from the measured  $I$ - $V$  relations in a straightforward manner. No a-priori, quantitative, information on defects concentration, i.e. on  $\delta$ , is required. Using the semi-empirical method also allows increased precision in the measurement of the ionic mobility by determining the mobility under different voltage sweep rates at a given temperature and taking the average. We illustrate this new approach by examining data obtained for 260 nm thin films of  $\text{MoO}_{3-\delta}$  [6].

## 2. Results

Previously it was shown that the  $I$ - $V$  relations in the metal/MIEC/metal devices exhibit frequency dependent dynamic negative differential resistance (NDR) and hysteresis for voltages higher than several  $k_{\text{B}}T/q$  ( $k_{\text{B}}$  - Boltzmann constant,  $T$  - temperature and  $q$  - elementary

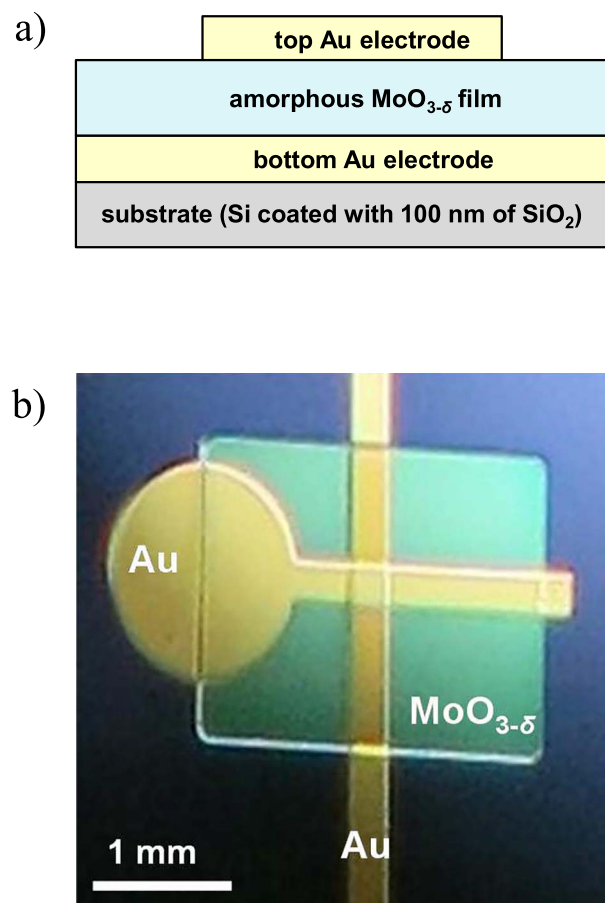


Fig. 1. a) Schematic of the cross section of the Au/ $\text{MoO}_{3-\delta}$ /Au device. b) Photo image of the top view of the device.

charge) [6,12]. In this work it is shown that these characteristic  $I$ - $V$  relations can be used for extracting ionic mobilities in thin film MIECs.

We revisit the experimental data presented in ref. [6] which were analyzed by the fitting method and apply them the new analysis method. Au/ $\text{MoO}_{3-\delta}$ /Au devices (Fig. 1) were prepared, in which the reduced, nonstoichiometric  $\text{MoO}_{3-\delta}$  contains significant concentrations of both mobile oxygen vacancies and electrons, as described previously [6]. This defect model for  $\text{MoO}_{3-\delta}$  was recently supported by measurements of the dependence of the total conductivity on the oxygen partial pressure (Brower diagram) for bulk samples of  $\text{MoO}_{3-\delta}$ , for which a slope of  $-1/6$  for a double logarithmic plot of the total conductivity versus oxygen partial pressure is observed [13]. The  $I$ - $V$  measurements used for extracting values for ionic mobility are performed in this study in the near to ambient temperature range of 55–75 °C in order to obtain values for the ionic mobility of  $\text{MoO}_{3-\delta}$ .

The first step in achieving an accurate measurement of the ionic mobility is finding an appropriate working frequency (or period) for the applied voltage, having a periodic triangular waveform, as in cyclic voltammetry. The amplitude of the applied voltage is much higher than  $k_{\text{B}}T/q$ , yet it is limited to avoid irreversible changes (oxygen loss, electroforming or break down) and to keep ionic mobility constant. The mobility becomes electrical field dependent under high electrical field when the electrical potential drop over a hopping distance exceeds  $k_{\text{B}}T/q$ . This requires an electrical field that exceeds  $10^6$  V/cm [14], while in this work the maximum applied electrical field is less than  $3 \cdot 10^4$  V/cm. For our  $\text{MoO}_{3-\delta}$  thin film, a maximum voltage of 0.6 V was found to allow for reproducible measurements with no measurable changes in the device during the relevant measurements [6]. The working frequency range (or working voltage sweep rate) of the device can be found from analyzing the one which results in significant hysteresis in

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