Chemical Nanoscale Analysis of Mesoporous Mixed IrOx-TiOy Thin Films

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1. Introduction

Porous films play an important role particularly in energy applications like photovoltaics, electrolysis, or batteries. Thin film properties such as thickness, chemical composition, crystallinity of the framework, and porosity define the activity of the porous films. The accurate morpho-chemical characterization of mesoporous thin films is a challenging analytical task which requires the consideration of new analytical approaches based on the combination of data of different methods able to address the structure and chemical composition at the nanoscale.

In this contribution we characterize thin mesoporous iridium-titanium mixed oxide film properties by EDS at an SEM applied in the dedicated "thin film analysis" approach [1]. Thus, the film mass deposition, film thickness and the film density can be determined [2]. Further, by dividing the measured film density to an assumed (theoretical) metal oxide framework (skeletal) density, the thin film porosity can be extracted, too [3,4].

2. SEM/EDS Analysis

To assess the lateral homogeneity of the morphology and chemistry of the mixed IrOx-TiOy thin films, first, high-resolution electron microscopy in conjunction with EDS elemental mapping have been applied on detached, free-standing films. Figure 1 shows an example of a mesoporous film with laterally inhomogeneous morphology, with islands-like structures of 150-200 nm size, of no templated mesoporosity, and which could be identified by EDS as IrOx-rich regions in the layer.

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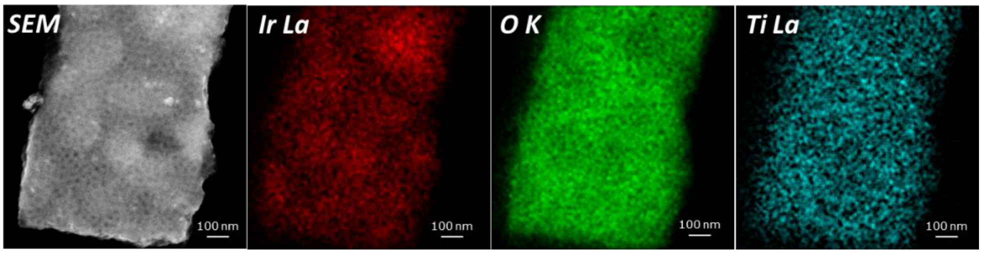

Figure 1: 5 kV SEM and EDS elemental maps of an IrOx-TiOx thin layer prepared as free-standing sample. Note the IrOx-rich domains within the mesoporous TiOx-rich matrix.

3. ToF-SIMS Analysis

A more surface and elemental sensitive analysis of the chemistry of a film like that presented in Figure 1, including a superior lateral resolution (of <100 nm) has been attained by mapping the sample surface with ToF-SIMS. Figure 2 displays the distribution of IrO+ and TiO+ ions at the surface of the film, demonstrating IrOx-rich islands observed with SEM and indicated by EDS in Figure 1. Further, the depth profiling mode of SIMS has been applied on homogeneous and inhomogeneous IrOx-TiOy films, revealing significant differences in the courses of Ir+, Ti+ and TiO+ ions along the film depth, with direct correlation to the synthesis conditions: the water content in the dip coating solution might lead to a separation of the IrOx and TiOy precursors, and provides a TiOy network with a templated mesoporosity and IrOx domains with a "native" porosity at the interfaces. In contrast, a dip coating solution without additional water results in an ordered pore network with a uniform distribution of IrOx and TiOy.

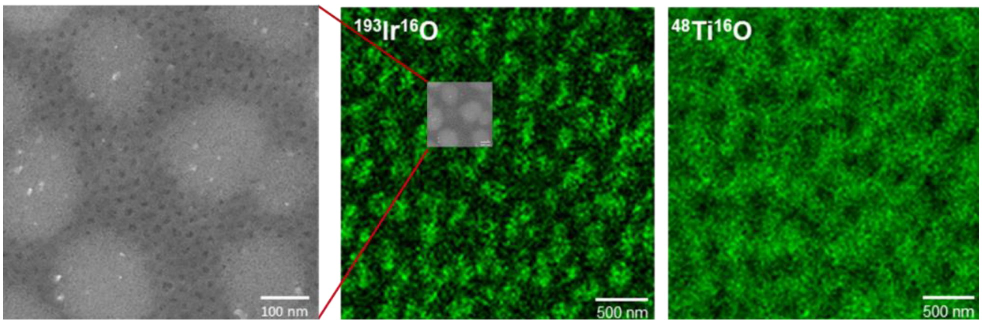

Figure 2: Chemical imaging of an IrOx-TiOx thin layer by ToF-SIMS. Note the IrOx-rich domains within the mesoporous TiOx-rich matrix at the surface.

4. Auger Electron Spectroscopy Analysis

Auger electron spectroscopy, with its excellent lateral resolution of <20 nm has been employed with the dedicated purpose of investigating the in-depth elemental distribution within the island-like structures in the inhomogeneous IrOx-TiOy films. The result of such an analysis is illustrated in Figure 3 and confirms basically the findings with ToF-SIMS. Slight enrichments of Ir are observed at the surface of the IrOx domains, but also at the interface thin film/ (Si) substrate in the IrOx-islands-free film matrix, the latter being accompanied by a decreased signal of oxygen.