Characterization of rhenium compounds obtained by electrochemical synthesis after aging process

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ABSTRACT

The proper identification of the molecular nature of the aged rhenium compound obtained by means of electrodeposition from an alkaline aqueous electrolyte was determined. Chemical, structural and vibrational experimental characterization of the aged Re compound showed agreement with quantum-computations, thereby allowing the unambiguous identification of the Re compound as $H(ReO_4)H_2O$.

1. Introduction

Rhenium (Re) and its compounds have been used in traditional applications for more than 40 years, mainly in the petroleum-reforming industry and in the production of special metal alloys [1]. In recent years, research on this material at nanocrystalline size has been focused on microelectronic applications (e.g. semi-conductors and thermoelectrics) [2–7]. In particular, rhenium oxides, primarily Re_2O_7, ReO_3 and ReO_2, have been studied for a range of applications, such as bimetallic catalyst systems, electro-chromic devices, rechargeable batteries and liquid crystal cells [8,9].

These materials have been largely obtained by means of chemical vapor deposition (CVD) [10,11], physical vapor deposition (PVD) [9,12], and wet chemical routes [13,14]. Some efforts have been made to explore the electrodeposition of rhenium and rhenium oxides on various substrates as a cheap and rapid process for the controlled manufacturing of nanocrystalline thin layers and bulk materials [15–18].

Most of the published literature has considered the electro-deposition of rhenium oxides from perrhenate ions (ReO_4^-) in acidic aqueous media [19–25], but information regarding the electrodeposition process in alkaline aqueous media is scarce. Recently, the authors have described an electrochemical strategy for the production of rhenium oxide nanostructured films from alkaline aqueous solutions, which led to the conclusion that Re, ReO_2 and ReO_3 coexist in the electrodeposited material [26,27].

Although it is known that rhenium oxides are highly reactive [25,28], there are no conclusive reports about the molecular structure of the electrodeposited material (i.e., from acidic or alkaline aqueous media) after an environmental aging process. The aim of the present work is to identify the molecular structure of the electrodeposited Re compounds from alkaline aqueous media after a 7 days aging process in air at room temperature and 40–80% relative humidity.

The proper identification of the nature of the aged rhenium compound is a key factor to be studied, not only because the molecular structure will determine the final properties of the electrodeposited material, but also for the development of better

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electrodeposited thin solid films with time-stable properties for the above mentioned applications. At present, the information regarding this issue is scarce and ambiguous which may lead to speculative conclusions about the performance of rhenium oxides. Therefore, this work attempts to provide an unambiguous analysis for solving this problem.

2. Experimental details

2.1. Electrochemical synthesis

As previously described [26,27], the electrochemical synthesis of rhenium compounds were made in a standard double jacket-glass electrochemical cell. The electrolyte was prepared by dissolving ammonium perrhenate in an alkaline aqueous solution at pH 13.3 ± 0.1 (0.125 mol dm^{-3} NH$_4$ReO$_4$+0.01 mol dm^{-3} NaOH) with deionized water. The electrodeposition was carried out in a standard two electrode cell (anode and cathode). A copper cathode (Cu, 99.9%) and a platinum anode (Pt, 99.9%) with an apparent surface area of 1.0 cm^2 and 4.0 cm^2 respectively were used. The anode–cathode separation was 24 mm and the galvanostatic electrodeposition was conducted with a 5 A–30 V GW rectifier. The cell potential during the experiment showed to be stable at 8.6 ± 0.7 V. The cell current density was about 770 A m^{-2} and it was maintained to a total deposition time of 1 h. A thermostatic bath was used to keep the temperature at 25 ± 0.2 °C inside the electrochemical cell and continuous bubbling of oxygen-free N$_2$, with 1200 rpm stirring, was used to eliminate oxygen in the solution. For the aging process, the samples were exposed in air at room temperature and 40–80% relative humidity for 7 days.

2.2. Density functional theory (DFT) computations

The computations were performed using the spin-unrestricted gradient-corrected DFT as implemented in the NWChem package [29]. The Perdew–Wang-91 (PW-91) exchange-correlation functional [30] and all-electron LANL2TZ basis sets [31] were employed, except for Re where a relativistic effective core potential was used to represent the 60-electron ionic core, and the LANL2TZ basis sets for the remaining 15 ($5s^25p^66s^25d^5$) valence electrons. These choices were based on the results of test computations performed for the Re atom and water molecule using a variety of alternative exchange-correlation functionals and/or basis sets. The structural optimizations, i.e. atomic and lattice parameters were performed using gradient-based techniques with no symmetry constraints imposed. The computations of IR vibrational normal modes were based on the harmonic analysis methodology and molecular models including 1, 2, and 4 formulas of H(ReO$_4$)H$_2$O atomic structure were used.

2.3. Materials characterization

The aged electrodeposited samples were characterized by several techniques:

Scanning electron microscopy (SEM) in a FEI-Quanta 250 FEG-ESEM operated at 20 kV and equipped with an Oxford energy dispersive X-ray analysis system.

Grazing-incidence X-ray diffraction (GI-XRD) was carried out in a Bruker D8 Advance diffractometer using Cu $K\alpha$1 radiation at $\lambda = 1.54$ Å; the angle of the X-ray source was kept at $1.5°$ with respect to the sample surface and the scanning angle range was $15°$–$90°$ with an increment of $0.02°$ and an accumulation per step of 1 s.

X-ray photoelectron spectroscopy (XPS) was carried out with a Perkin Elmer PHI 1257 spectrometer using non-filtered Al-$K\alpha$ radiation with $h\nu = 1486.6$ eV, a take-off angle of the emitted photoelectrons set to $45°$ with respect to the sample surface normal and a chamber pressure of 10^{-7} Pa. The internal calibration of the binding energy (BE) of the XPS spectra was made by using the C-1s line of adventitious carbon, setting it at 284.8 eV. The accuracy of the BE scale was ± 0.1 eV. In order to accurately determine the BE of the different element core levels, high resolution spectra were always fitted using Gaussian–Lorentzian curves. Prior to curve fitting, the background curve was subtracted by the method devised by Shirley [32].

Raman spectroscopy (RS) was used to study the samples in two different spectrometers: (a) on a WITec alpha300R model CRC200 using a diode laser of 10 mW with a wavelength of 633 nm and (b) on a triple monochromator Jobin Yvon Inc. T64000 using a Coherent Innova 99 Ar$^+$ laser with a radiation of 514.5 nm. Both spectra were recorded in a backscattering geometry at room temperature. Finally, vacuum-dried samples were analyzed on a Rayleigh WQF-510A FTIR spectrophotometer; spectra were also taken from vacuum-dried KBr samples.

3. Results and discussion

The present approach involves the experimental characterization of the synthesized material by various techniques described below, and further comparison with quantum mechanical computations carried out by means of density functional theory (DFT). Fig. 1 shows scanning electron microscopy (SEM) images of the electrodeposited material on a copper substrate after the aging process. The micrographs revealed a smooth surface of the electrodeposited material at microscopic level and the high magnification image shows that the material surface exhibits a globular morphology; the latter indicates that the growing process during the electrocrystallization is controlled by ReO$_4^-$ diffusion. It is possible to observe tiny cracks due to the presence of the parallel hydrogen evolution reaction (HER) during the
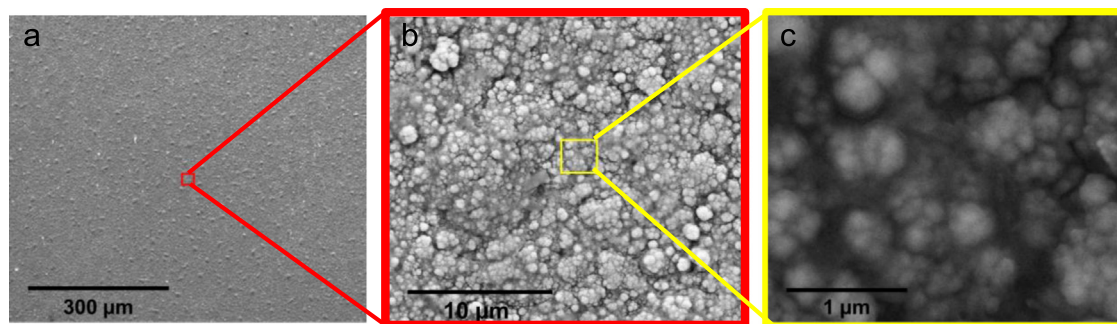
Fig. 1. SEM images of the aged electrodeposited material on a copper substrate: (a) low magnification secondary electron image, (b) a combined secondary and backscattered electron image showing the crack formation in the electrodeposited material and (c) high magnification secondary electron image of the synthetized material.