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X-ray excited Auger Cu L₃L_{4,5}M_{4,5} spectra measured at low take-off angles as a fingerprint for a Cu-organics connection

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ABSTRACT

In this work, surface analysis by measuring high-resolution Auger Cu L₃L_{4,5}M_{4,5} spectra was performed at very low take-off angles using X-ray photoelectron spectroscopy. The focus of this research was on determining if a fingerprint feature exists for a specific connection between Cu(I) (and/or Cu(II)) and different organic molecules. These organic molecules were adsorbed on Cu surface from 3 wt.% NaCl solution containing a 1 mM concentration of organic compound, i.e. 4-methyl-2-phenylimidazole, benzotriazole, 3-amino-1,2,4-triazole, 1,2,4-triazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 1-hydroxybenzotriazole, and 2-mercapto-1-methylimidazole. This feature was shown to be connected to Cu(I)- and/or Cu(II)-complex formation.

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1. Introduction

The analysis of the very thin surface layers of a certain system is frequently challenging. Few analytical techniques are able to provide specific information about the thickness of thin surface layers, the manner of bonding of certain species with the substrate, and even more importantly, a specific fingerprint for a certain adsorbate/substrate connection on the surface. X-ray photoelectron spectroscopy (XPS) is probably the currently most widely employed surface analytical technique that can provide such information [1–3].

In this work, a specific fingerprint feature for certain species that adsorbed on the Cu surface was explained by means of the XPS method. The adsorbed compounds on Cu surface presented in this work were corrosion inhibitors [4–6].

In an XPS analysis, the take-off angle (θ) is considered to be the angle with respect to the sample surface. The analyzed depth in the XPS analysis is defined as the depth from where 90% of the XPS signal originates and is calculated as $3 \cdot (\text{IMFP}) \cdot \sin(\theta)$, where IMFP is the inelastic mean free path for electrons. Therefore, the topmost species are analyzed at the lowest θ . On this basis, primarily θ of 5° , and also 20° for comparison, were employed herein in order to analyze the topmost species on the Cu surface. This procedure proved useful for revealing the corrosion inhibitor and Cu substrate

connection. The main focus of this work was to determine if a certain connection can be predicted by the analysis of the XPS-excited Auger Cu LMM spectrum.

It is well known that compounds containing N and S are potential corrosion inhibitors for Cu and also other metals. It was reported previously that 4-methyl-2-phenylimidazole (MePhI) [7], benzotriazole (BTAH) [8], 3-amino-1,2,4-triazole (3-AT) [9], 2-mercaptobenzimidazole (MBIH) [10], 2-mercaptobenzoxazole (MBOH) [11], and 2-mercaptobenzothiazole (MBTH) [12] are effective Cu corrosion inhibitors in chloride solution. 1,2,4-triazole (TRZ) compound could also act as a Cu corrosion inhibitor [9]. On the other hand, 2-mercapto-1-methylimidazole (MMel) showed corrosion inhibition effectiveness only for short-term immersion periods [13], whereas it loses its effectiveness after longer-term immersion periods. Furthermore, it was reported that BTAOH cannot be considered to be an effective Cu corrosion inhibitor [14]. Based on this data, the reason why this occurs is explained by means of the XPS method applied herein.

The purpose of performing sample immersion for 1 h is to analyze only the connection of organics and the Cu-substrate, otherwise corrosion inhibitor crystallites are formed [15,16] that are too thick for XPS analysis (a typical XPS analysis is performed for 1–5 nm thick surface layers). Complexes that are formed between Cu(I) and organics are known (from other fields of chemistry) and it is frequently explained that Cu(I) is formed when Cu corrodes in chloride solution and eventually bonds with a specific organic compound [17–19]. Moreover, Cu(II)-organic complexes have also been reported frequently [20–22]. Fig. 1 shows the structures of the cor-

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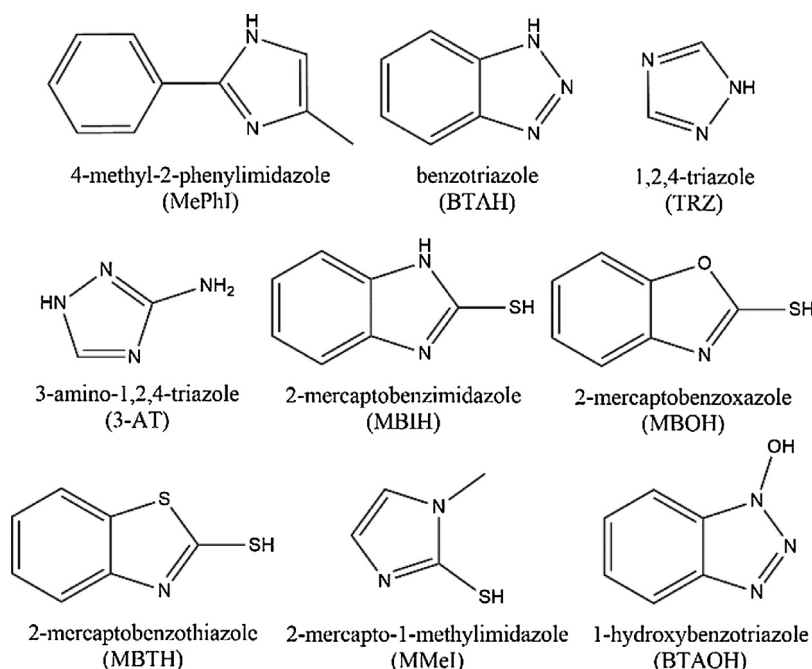


Fig. 1. Structures of the compounds that were adsorbed and XPS-analyzed on the Cu surface.

rosion inhibitors employed herein that adsorbed on the Cu surface and were subsequently analyzed. These compounds were selected in order to compare the influence of phenyl, methyl, and mercapto groups in the case of MePhI and MMel compounds, the influence of a benzene ring, a hydroxyl group, and the position of the N atoms in the case of BTAH, TRZ, 3-AT, and BTAOH compounds, and the influence on the position of heteroatoms in the MBIH, MBOH, and MBTH compounds on the Auger Cu $L_{3,4,5}M_{4,5}$ spectra.

Hitherto, to the best of the author's knowledge, such a systematic spectroscopical comparison had not been performed previously.

2. Materials and methods

2.1. Solution and material preparation

Copper foil, temper half hard, was purchased from Goodfellow (Cambridge, UK). The purity of the copper was 99.999 wt.%, as specified by the supplier. The samples for the XPS analysis were disc-shaped Cu samples 15 mm in diameter which were cut from the copper foil. The samples were ground under a stream of water using SiC papers and a rotating device, both provided by Struers (Ballerup, Denmark). Grinding was performed in sequence with 1200-, 2400-, and 4000-grit SiC papers. The grinding direction was changed four times by 90° to minimize abrasion. Finally, the samples were thoroughly rinsed with ultrapure water obtained from Milli-Q system (Millipore Corporation, Massachusetts, USA) with a resistivity of 18.2 M Ω cm at 25 °C. Afterwards, they were cleaned in an ultrasound bath containing 50 vol.% ultrapure water and 50 vol.% pure ethanol, again thoroughly rinsed with ultrapure water, and dried under a stream of argon. Immersion was performed at 25 °C controlled by a thermostat.

Solutions containing 3 wt.% NaCl solutions were prepared using ultrapure water. NaCl and ethanol (for analysis ACS quality) were obtained from Carlo Erba Reagents (Milan, Italy). The purities of the corrosion inhibitor chemicals were specified by the supplier: MePhI (95.0 wt.%) and MBIH (98 wt.%) from Sigma Aldrich (USA), and BTAH (99.0 wt.%), MBTH (98.0 wt.%), TRZ (99.5 wt.%), 3-AT (95.0 wt.%),

MBOH (99.0 wt.%), MMel (99.0 wt.%), and BTAOH (98.0 wt.%) from Acros Organics (USA).

2.2. XPS analysis

A PHI 5700 spectrometer with an Al K_{α} X-ray radiation monochromatic source (1486.6 eV) was employed. Using a hemispherical electron analyzer, the energy of the photoelectrons was measured at a pass energy of 187.8 eV for survey spectra and 29.3 eV for high-resolution XPS-excited Auger Cu $L_{3,4,5}M_{4,5}$ spectra. The high-resolution spectra were measured at θ of 5° and 20°, and survey spectra were measured at θ of 45°. The analyzed area comprised a spot with a radius of 0.4 mm. After collecting the spectra, Shirley [23] background subtraction was applied. In order to obtain a spectrum representing pure Cu, sputtering was performed by Ar⁺ ion beam (energy of 1 keV) on a 4 by 4 mm area.

3. Results and discussion

3.1. Survey spectra analysis

Fig. 2 shows the survey spectra for the Cu samples treated with different corrosion inhibitor solutions and the survey spectrum for Ar-ion sputter-cleaned pure Cu. The latter shows characteristic peaks for pure Cu, i.e. Cu 3p, Cu 3s, and Cu 2p peaks, and XPS-excited Auger Cu $L_{3,4,5}M_{4,5}$, $L_{3,2,3}M_{4,5}$, and $L_{3,2,3}M_{2,3}$ peaks. The indication that a corrosion inhibitor was adsorbed on the surface after treatment in a corrosion inhibitor solution arises from the fact that new peaks for C 1s and N 1s appear on the survey spectra (all compounds tested had N and C atoms in their structure, see Fig. 1). However, the C 1s peak could also originate from adventitious carbon species that adsorbed on the surface from the surroundings during sample preparation and the drying procedure. On the other hand, adventitious carbon can be employed to correct the E_B scale due to the charging effect (the binding energy (E_B) scale for all spectra was corrected to 284.8 eV using the advantageous carbon C 1s peak). In the case of mercapto compounds (MBIH, MBOH, MBTH, and MMel), additional S 2s and S 2p peaks are present in the survey spectra for these sample solutions. This is another indication

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