New Frontiers in Chemical State Analysis Using X-ray Photoelectron Spectroscopy (XPS)

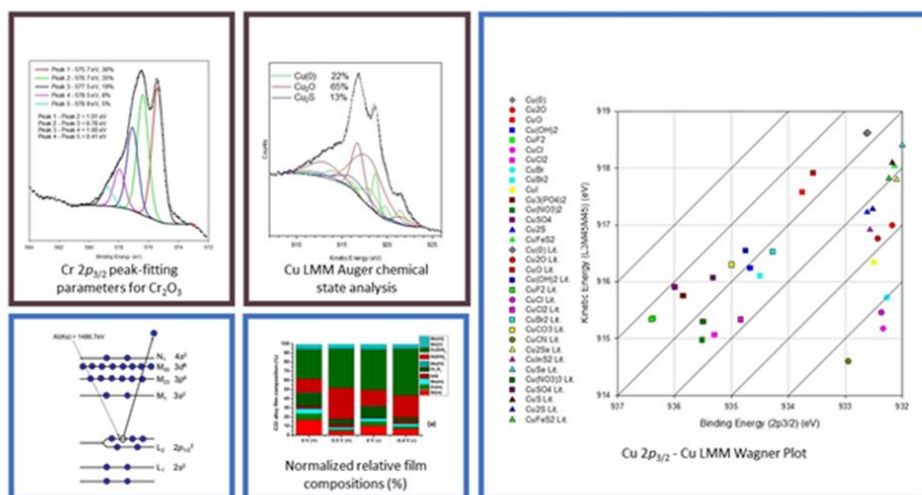Mark C. Biesinger[1]
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Résumé:
Chemical state XPS analysis of first row transition metals and their oxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work [1-5] has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis. There are numerous cases in the literature where lack of understanding of these parameters has led to erroneous interpretation of XPS data. This is particularly true in cases where species show significant multiplet splitting e.g. Cr, Mn, Fe, Co and Ni. A more consistent, practical and effective approach to curve fitting has been developed. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu, have also been shown to be of use for chemical speciation.

Cr $2p_{3/2}$ peak-fitting parameters for Cr_2O_3

Cu LMM Auger chemical state analysis

Normalized relative film compositions (%)

Cu $2p_{3/2}$ - Cu LMM Wagner Plot

Abstract:
Chemical state XPS analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. An overview of XPS analysis and curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.

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