X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), or Electron Spectroscopy for Chemical Analysis (ESCA) is a quantitative method to determine the elemental composition of surfaces and surface layers. In addition, XPS provides information on molecular bonding states and layer thickness.

In XPS, a sample is irradiated by monochromatic X-rays which leads to the emission of photoelectrons from the excited atoms (see Figure 1). A hemispherical energy analyzer is used to measure the kinetic energy of these electrons and the element-specific binding energies (E_B) are calculated according to the equation:

$$E_B = h\nu - E_K - \phi$$

where $h\nu$ is the X-ray energy (e.g., Al Kα energy $h\nu$=1486.6 eV), E_K is the photoelectron kinetic energy, and ϕ is the work function of sample and the spectrometer. With XPS, all elements (except H and He) can be identified and quantified. In addition to elemental composition, XPS can provide bonding state information based on chemical shifts (see Figure 2). The binding energy of an element depends on its chemical environment. That is, non-equivalent atoms of the same element in different oxidation states or different molecular environments give rise to shifts in the measured binding energy. XPS is surface sensitive because only electrons from the top 5 – 10 nm can leave the sample surface without further energy loss. The detection limits of XPS depend on the element and are typically between 0.1 – 1 atom percent.[1]

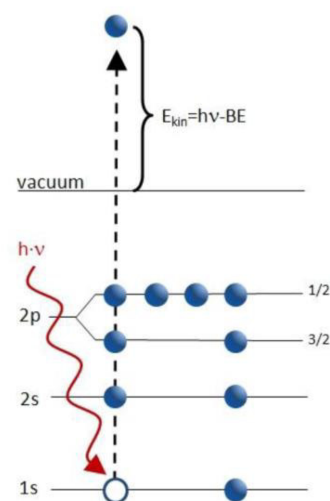

Figure 1 Excitation of photoelectrons in XPS (photoelectric effect)

Properties of XPS:

- Qualitative and quantitative elemental composition with detection limits of 0.1 atomic percent
- Oxidation state and molecular information by chemical shifts
- Information depth of 5 – 10 nm
- Suitable for all solid samples

Operational Modes:

- Spectra (overview and detail)
- Line scans (series of spectra)
- Chemical images (spatial resolution of > 8 µm
- Thickness analysis by model-based analyses or angle-resolved XPS
- Depth profiling

[1] Briggs and Seah, Practical Surface Analysis, 1983

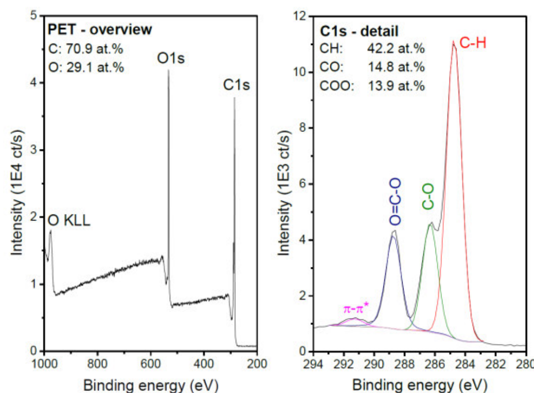

Figure 2 XPS survey and C1s high-resolution spectra of PET.

Figure 2 shows an example of an overview (survey) spectrum and a carbon 1s high-resolution spectrum acquired from a poly(ethylene terephthalate) (PET) reference sample. Based on the survey spectrum, the elements can be identified and quantified (see the concentration information in Figure 2). The carbon 1s high-resolution spectrum provides more detailed quantitative information about the carbon bonding states for PET: 1) C-C,C-H; 2) C-O, 3) COO, and 4) π-π* characteristic of aromatic materials.

XPS is a commonly used standard method for surface analysis. In addition to spectroscopy on selected surfaces, line scans are often used as the acquisition mode in the characterization of discontinuous or material transitions. In this case, XPS spectra are recorded along a predetermined line. The combination of chemical and lateral information makes it possible to draw conclusions about the distribution of chemical substances over the surface.

Modern XPS instruments also offer the possibility to provide chemical maps of a surface. For example, Figure 3 shows an XPS analysis of the cross-section of a fuel-cell membrane. The SEM image is included for comparison purposes. The polymer-based membrane in the center of the image is surrounded by platinum containing coatings. This layer system is stabilized by a phosphor containing support. The structure of the membrane system is clarified in the XPS overlay of P (red) and Pt (green). Based on these data, the exact composition of the Pt coatings can be determined quantitatively.

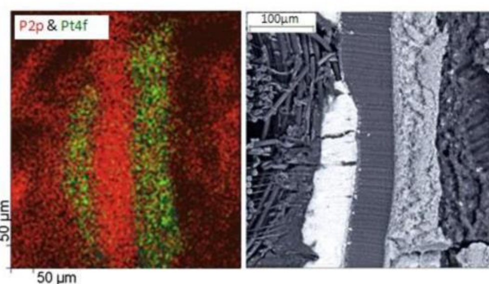

Figure 3 Cross-section of a fuel cell membrane (left XPS Overlay; right SEM image)

In addition to spectroscopy of the surface and imaging the lateral distribution of components, XPS can be used to determine the layer structures as a function of depth (depth profiling). For example, a model-based calculation can be used to determine the oxide layer thickness from oxide layers with a thickness below the XPS information depth. In addition, the angle between the sample and the analyzer can be varied to alter the information depth. This angle-resolved XPS (AR-XPS) experiment can also be used to identify the layer structure. For thicker layers, the classic XPS depth profiling experiment can be conducted to evaluate the composition as a

function of Ar^+ ion sputtering. Figure 4 shows such an XPS depth profile of an oxide layer at the interface of an Al contact to an organic light emitting diode (OLED). The data clearly show an accumulation of magnesium and oxygen at the interface between contact and the organic electronics.

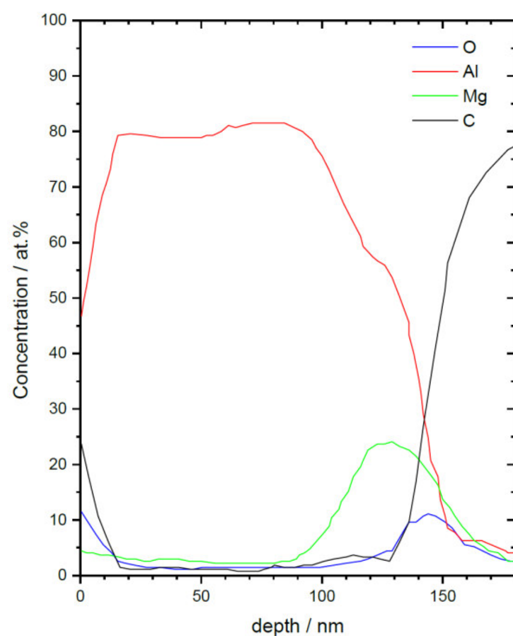

Figure 4 XPS depth profile of an Al contact for an organic light emitting diode (OLED)