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Novel Energy Materials Research With X-ray Photoelectron Spectroscopy

*X-ray photoelectron spectroscopy at **TLS 24A1** helps researchers identify the chemical composition at the surface/interface of new energy materials.*

TLS 24A1 provides a wide-range soft X-ray beamline with photon energies ranging from 15 to 1600 eV. X-ray photoelectron spectroscopy (XPS) is the primary application of this beamline. **TLS 24A1** is equipped with two endstations: an ultra-high vacuum XPS for standard surface analysis and a near-ambient-pressure XPS (APXPS) to characterize surfaces in sub-Torr pressure ranges. The versatility of XPS has attracted multidisciplinary research groups to conduct experiments at **TLS 24A1**. Here, we highlight five papers which reported the development of novel materials with an emphasis on the role of XPS.

The global energy crisis has resulted in recent research efforts devoted to solid-state batteries. The interface at the electrolyte–electrode boundary is a crucial factor that determines battery performance. The following three examples of Bing Joe Hwang, Wei-Nien Su (both from National Taiwan University of Science and Technology) and their collaborators demonstrate the role of XPS in elucidating the chemical composition around the electrode–electrolyte interface. The first example is the development of anode-free lithium metal batteries containing a lithium argyrodite solid-state electrolyte.[1] To enhance the contact between the solid-state electrolyte and the Cu@Ag of the outer circuit, a deformable sulfide composite solid electrolyte (SCSE-4) was fabricated by incorporating the common lithium argyrodite (LPSC) into a eutectic solution with a polyvinylidene fluoride binder and LiF salt additive. XPS shows that the thiophosphate group in the SCSE-4 composite retained its identity in the eutectic mixture, indicating that the void volume in the sulfide composite solid electrolyte is negligible. Consequently, the contact between the solid-state electrolyte and the outer circuit is enhanced. In the second example, the research team synthesized a novel, highly fluorinated electrolyte to mitigate the capacity fading of high-voltage lithium-ion batteries.[2] XPS confirms that the fluorinated electrolyte effectively stabilizes both S-C(PAN) anode and LNMO cathode surfaces in the fuel cell. Lastly, the research team developed a new type of solid-state electrolyte made of iodized-oxychloride argyrodite.[3] The sacrificial iodine in the electrolyte effectively suppresses dendrite formation. XPS confirmed the synergistic contribution of sacrificial iodine and oxygen-doped sulfide solid electrolytes in forming a stable interface.

Aside from solid-state batteries, Hwang and Su's team attempted to enhance the electrochemical performance of a Zn aqueous battery by improving the uniformity of the Zn deposit.[4] Adding a low concentration of glutamic additive modifies the electrode surface's hydrogen-bonding network. Consequently, a uniform layer of Zn deposit is established on the electrode. In this work, XPS confirmed the binding of the glutamic additive on the surface.

Dye-sensitized solar cells have been intensely researched to enhance the harvesting of solar energy. Eric Wei-Guang Diau (National Yang Ming Chiao Tung University) and his collaborators developed X-shaped quinoxaline-based organic dyes, which serve as a p-type self-assembly mono (SAM) layer for tin perovskite solar cells.[5] The device performance reached 8.3% when the dye TQxD was used to construct the SAM layer, a record-high efficiency for SAM-based tin perovskite solar cells. In this work, the functional groups identified in the C 1s XPS confirm the chemical bonding between the SAM layer and the ITO substrate. (Reported by Bo-Hong Liu)

*This report features the work of Bing Joe Hwang, Wei-Nien Su, and their collaborators published in J. Power Sources **556**, 232462 (2023); J. Power Sources **558**, 232567 (2023); Nano Energy **112**, 108471 (2023); and ACS Appl. Mater. Interfaces **15**, 7949 (2023); as well as the work of Eric Wei-Guang Diau and his collaborators published in Adv. Funct. Mater. **33**, 2213939 (2023).*

TLS 24A1 XPS, UPS, XAS, APXPS

- XPS, UPS
- Materials Science, Batteries, Catalysts

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Hold the Sun in the Palm of Your Hand

Microbeam GIWAXS is used in the study of solar cells.

A thin film is a layer of material deposited or coated on substrates with a thickness in the range of nanometers to a few micrometers. X-ray scattering methods are frequently used for thin film analysis. Due to the thickness of thin films and the existence of substrates, the transmission geometry of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) is limited. Therefore, grazing-incidence small-angle X-ray scattering (GISAXS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) are extensively applied in thin film structural analysis. In the geometry of grazing incidence, an X-ray beam impinges on the surface of a thin film with an angle close to the total reflection angle, thereby increasing the penetration path in the sample. In-plane and out-of-plane structures of thin film are extracted from X-ray scattering patterns that are collected by two-dimensional X-ray detectors.

TPS 25A is capable of performing transmission and grazing-incident SAXS/WAXS. The total X-ray photon flux at the sample position is approximately 10^{12} photons/second and the vertical and horizontal beam sizes at the sample position are approximately 3 and 5–10 μm, respectively. With the typical incident angle (*i.e.*, 0.05°), the footprint on the thin film is about 5 mm. The sample stage is composed of a hexapod and a stand for thin films. The six-axis positioning system provides with submicron precision and rigid stability. For scattering pattern collection, the instrument is equipped with two area X-ray detectors, a Dectris EIGER X 1M and 16M. The 16-megapixel detector is for SAXS/GISAXS and the smaller, 1-megapixel detector is for WAXS/GIWAXS. With the incident X-ray photon energies in the range of 5.4 to 20 keV, the q-range with the small-angle detector covers 0.0007 to 0.7 $Å^{-1}$. An order-of-magnitude of two in the q-range can be achieved in one acquisition. For wide-angle experiments, the q value is up to 5 $Å^{-1}$.

For an isotropic SAXS sample, the magnitude of the momentum transfer can be expressed as:

$$q = \frac{4\pi}{\lambda} sin\left(\frac{2\theta}{2}\right)$$

where 2θ is the scattering angle and λ is the wavelength ofthe incident X-ray. In grazing-incidence geometry, the vector components must be taken into account:

$$q_x = \frac{2\pi}{\lambda}\left[cos\, cos\,(\alpha_f)\, cos\, cos\,(2\theta_f) - cos\, cos\,(\alpha_i)\right]$$

$$q_y = \frac{2\pi}{\lambda} cos\, cos\,(\alpha_f)\, sin\, sin\,(2\theta_f)$$

$$q_z = \frac{2\pi}{\lambda}\left[sin\, sin\,(\alpha_f)\, sin\, sin\,(\alpha_i)\right]$$

where x, y, and z are the in-plane direction, beam direction, and out-of-plane direction, respectively, α_i is the incident angle, α_f is the out-of-plane scattering angle, and $2\theta_f$ is the in-plane scattering angle.