

# The use of the X-ray absorption near edge spectrum in materials characterisation

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## Abstract

The increasing availability and use of synchrotron radiation has opened up new horizons in materials research. These sources offer very high brightness photon probes in an unparalleled wavelength range from the UV to the hard X-ray region. Although the medium to hard energy extended X-ray absorption fine structure (EXAFS) has been widely used in materials characterisation, the near edge absorption spectrum (XANES), especially in the soft X-ray region below 2 kV, has been exploited to only a limited degree. This relates to both the difficulties and limited availability of soft X-ray monochromators and the complexity of the spectra relative to the EXAFS region. We have used XANES in studies of semiconductor oxide and nitride materials, the speciation of sulfur in industrial smelting anodes and the development of oxide based electrode materials for Li ion batteries. Although of limited quantitative applicability, the chemical detail available in these spectra is considerably superior to that in the X-ray photoelectron (XPS) spectrum and demonstrates the considerable power of the method.

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## 1. Introduction

The announcement in 2001 that an Australian Synchrotron will be built by the State of Victoria, at a site near Monash University [1] has awakened considerable interest on both sides of the Tasman, in the uses of synchrotron radiation. This facility will become part of a burgeoning international array of such instruments, driven by the demand for ultra-bright, broad-spectrum radiation across a growing range of disciplines. The extreme brightness, high collimation and variable polarisation characteristics of such radiation offers a unique probe of the compositional, chemical, magnetic and electronic properties of materials, at resolutions approaching the nanoscale.

In materials science, interest has historically centred on the harder X-ray region, where both structural

studies using diffraction, or absorption in the extended X-ray absorption fine structure (EXAFS) region, have dominated. More recently there has been increasing use of the near edge region (0–50 eV above edge) of the soft X-ray (<2 kV) absorption spectrum. Although complex to interpret, this region, where the orbital energies probed are comparable to those considered in conventional X-ray photoelectron spectroscopy, offers a richness of chemical detail not accessible in the more structurally useful extended (>50 eV above edge) region of the harder X-ray absorption spectrum. Such measurements are rarely used in combination at the same edge, as the EXAFS measurement requires a clear energy window extending several hundred eV above the edge and this is uncommon in the soft X-ray region. Thus the latter tends to be concentrated on the harder energy edges.

For a number of technical reasons diffraction grating based monochromators which operate in the 100–1800 eV range are far less common than the crystal diffraction based devices operating at higher energies, thus the

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accessibility of this form of spectroscopy has lagged some way behind the more mature EXAFS approach. Whereas the EXAFS region is dominated by single scattering effects where a sophisticated theoretical analysis is available, the multiple scattering effects and complexity of the band structure immediately above the band-gap or Fermi edge make the XANES region significantly more difficult to interpret [2].

## 2. Results and discussion

Recent experiments carried out by our group at the Canadian Synchrotron Radiation Facility, located at the Synchrotron Radiation Centre of the University of Wisconsin, Madison, have demonstrated the remarkable versatility of the XANES spectrum. These have included studies of lithium manganese based battery materials, where a critical issue is the oxidation state changes of the transition metal species during battery cycling. The ability of the photoelectron spectrum to distinguish especially between  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  has been a problem, however the XANES of the transition metal L edge clearly resolves this issue in a number of cases where competitive oxidation state changes are possible (Fig. 1). In mixed Li, Mn, Cr oxide systems, it has been demonstrated that  $\text{Mn}^{4+}$  is stable with respect to Li cycling of the material, while Cr is the electroactive species [3]. This is important for these materials in limiting the Jahn–Teller distortion arising from the  $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$  transition. In pure Li manganates this transition breaks down the structure and limits the life of the material [4].

The international aluminium industry consumes some 10 M tonnes of petroleum coke in the consumable anodes used in the reduction cell. Petroleum cokes, a

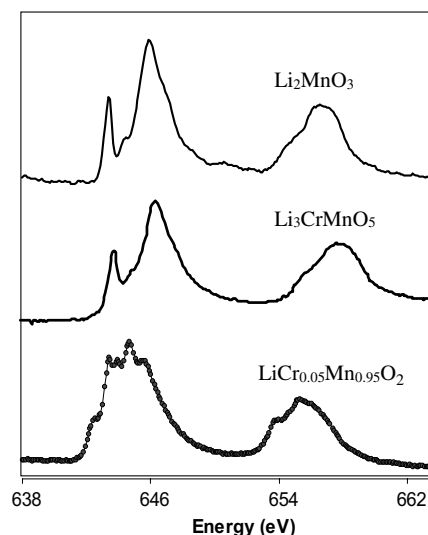


Fig. 1. Mn L-edge XANES spectra of a  $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$  cathode material, the 50:50 Cr:Mn structure  $\text{Li}_3\text{CrMnO}_5$ , and a standard  $\text{Mn}^{4+}$  compound  $\text{Li}_2\text{MnO}_3$ .

residual product of crude oil processing, typically contain between 1 and 4 wt% sulfur, an amount which is steadily increasing as more sour crudes are processed [5]. The speciation of this S in the anode is important in understanding the generation of sulfur gases in the reduction cell. Carbonyl sulfide (COS) has been identified as the dominant sulfur containing gas released at the anode surface [6]. Reaction with atmosphere above the electrolyte surface converts most COS into  $\text{SO}_2$  and  $\text{CO}_2$ , but some survives to escape, ultimately into the atmosphere [7].

S K edge ( $\sim 2500$  eV) and L edge ( $\sim 164$  eV) spectra have been collected from a variety of petroleum cokes, baked anodes and anode butts recovered after use.

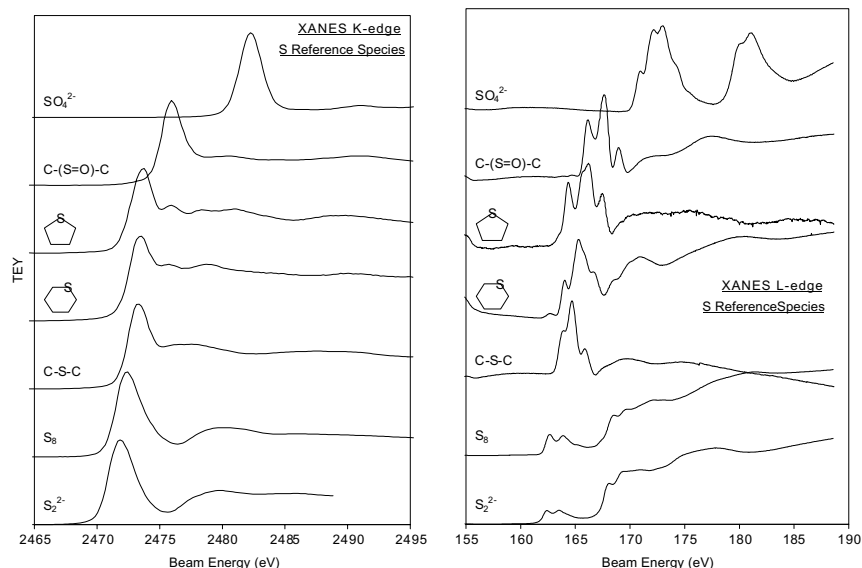


Fig. 2. Total electron yield XANES spectra scanning photon energies over the S K edge (left) and the S L edge (right).

These spectra have been compared with those from a suite of model compounds. The K edge spectra show little distinction, other than a well resolved oxidation state determined peak shift (Fig. 2). However the L edge spectra reveal detailed fingerprints of the model compounds and the anode materials, confirming that 5- and 6-membered ring structures dominate the S speciation in all these materials (Fig. 3). Furthermore, even in the relatively oxidising environment in the residual anode butt, these species are stable to well beyond both the normal anode baking temperature (1100 °C) and cell operating regions (up to 1000 °C) [7,8].

Perhaps the most detailed study has been the examination of the N K edge spectrum in amorphous ion assisted deposition (IAD) deposited GaN thin films [9]. These studies reveal exceptional chemical detail with the surprising revelation of the complete vibrational spectrum of molecular nitrogen (Fig. 4) trapped in these films. This result is remarkable in that in films of <150 nm, this species appears to be extremely prominent, in both the total electron yield (TEY) and fluorescence spectra, with analysis depths of ~5 nm and ~70 nm respectively. This poses the question of how so much interstitial molecular nitrogen can be loaded into such films and remain stable with respect to annealing treatments. The crucial attribute of the synchrotron result is energy resolution over an order of magnitude superior to that of the conventional X-ray photoelectron spectrum. The additional information offered in the XANES spectrum has been spectacularly useful in this case in

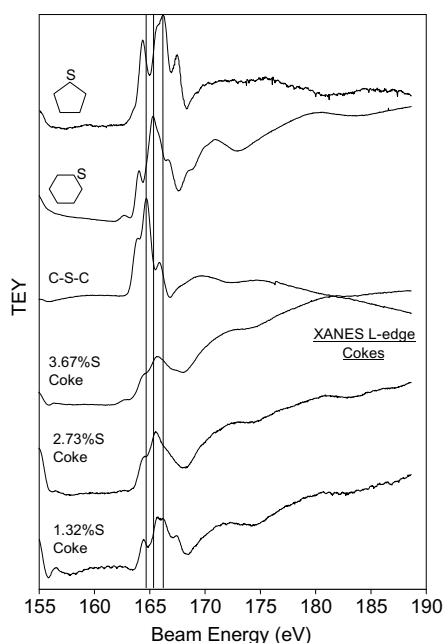


Fig. 3. Total electron yield S L edge XANES spectra over the photon energy range of 155–190 eV. A number of petroleum cokes (lower spectra) are compared to selected reference compounds indicating the dominance of 5- and 6-membered ring structures.

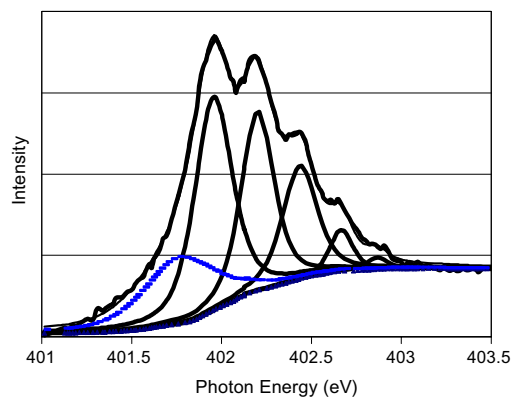


Fig. 4. The vibrational spectrum of molecular nitrogen, observed in the N K edge XANES spectrum of an amorphous GaN thin film.

clearly identifying the narrow peak superimposed on what is otherwise a typical spectrum of crystalline gallium nitride [10,11].

### 3. Conclusions

These results, spread across a variety of materials science applications demonstrate the usefulness of the X-ray absorption near edge spectrum in providing detailed chemical and some micro-structural information. Three separate beamlines have been used in photon ranges of 100–300 eV (Grasshopper), 250–700 eV (spherical grating monochromator) and 1.2–4 keV (double crystal monochromator) to examine transitions from core levels ranging from the S L edge to the S K edge. The synchrotron measurements offer an unparalleled combination of sensitivity and extreme energy resolution (better than 100 meV for the SGM) and have resolved a number of crucial research questions largely in chemical speciation. These include the nature of S in carbon smelting anodes, nitrogen in IAD deposited GaN, and oxidation states of metal ions in complex mixed metal oxides battery materials. These methods offer complementary information to the more structurally illuminating measurements in the harder X-ray EXAFS region. The increasing development and interest in monochromators operating in the soft X-ray region is fuelling much more use of this particularly useful near edge region of the X-ray absorption spectrum.

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