

# Recent advances in dual mode charge compensation for XPS analysis

Lee Edwards<sup>1</sup> | Paul Mack<sup>2</sup> | David J. Morgan<sup>1,3</sup> 

<sup>1</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK

<sup>2</sup> Thermo Fisher Scientific, Birches Industrial Estate, East Grinstead, West Sussex, UK

<sup>3</sup> G.63 Research Complex at Harwell (RCAH), HarwellXPS—The EPSRC National Facility for Photoelectron Spectroscopy, Didcot, UK

## Correspondence

David J. Morgan, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, UK.  
Email: morgandj3@cardiff.ac.uk

## Funding information

Engineering and Physical Sciences Research Council (EPSRC), Grant/Award Number: PR16195

Dual mode charge compensation has been used successfully for many years to enable X-ray photoelectron spectroscopy (XPS) analysis of a variety of insulating samples. This approach uses a combination of low energy electrons and argon to compensate for positive charge build-up during irradiation by X-rays. Whilst this method works with no detectable side effects in most cases, it was recently reported that the chemical bonding states of some Cr(VI) oxides may be modified by prolonged exposure to the flood source. In this work, we demonstrate successful dual mode charge compensation of CrO<sub>3</sub> with no discernible sample modification from the flood source. Under the same flood source conditions, we extend the analysis to other systems known to undergo reduction and present charge compensated XPS data for V<sub>2</sub>O<sub>5</sub> and a copper-based metal-organic framework (MOF) showing little or no modification from the flood source, even with prolonged exposure.

## KEYWORDS

argon, charge, compensation, electron, neutralisation, XPS

## 1 | INTRODUCTION: WHY USE DUAL MODE CHARGE COMPENSATION?

Electron ejection via photoemission is the underlying basis of X-ray photoelectron spectroscopy (XPS); therefore, for meaningful analysis of surfaces by XPS, the net positive charge on the surface from this emission must be balanced. For conducting materials in electrical contact with the spectrometer, replacement of these ejected electrons occurs naturally, whilst for electrically insulating materials, the positive charge cannot be dissipated and steadily increases until no more electrons can be ejected due to the increased energy required to overcome their orbital binding energy and the new charge state at the surface.

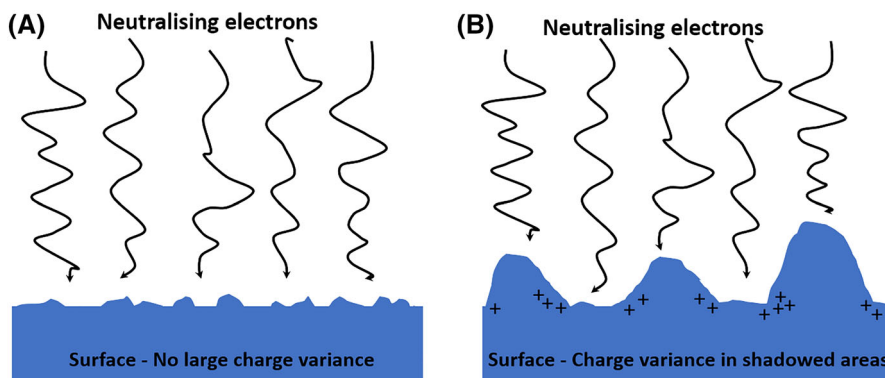
Typically, for nonmonochromatic X-ray sources, the thin aluminium window which separates the source from the sample surface allows for discrete neutralisation of insulating surfaces by creating a rich source of secondary electrons in the vicinity of the analysis area.<sup>1</sup>

Monochromatic X-ray sources, however, minimise stray secondary electrons due to the indirect illumination of the surface by the source, and any spectrum from an insulating material will gradually shift to higher binding energies becoming a mixture of broadened and displaced peaks making chemical state identification misleading or impossible, unless an external charge compensation source is used.<sup>1,2</sup>

Minimisation of this surface charge is typically achieved by thermionic emission, where low energy, negatively charged electrons from a heated filament flood the surface and compensate the positive charge. The surfaces illustrated in Figure 1 are presented to highlight a typical “flat” surface (Figure 1A), where the surface topology is relatively smooth, and so the flood electrons can neutralise the positive charge with relative ease. Figure 1B however illustrates a much rougher surface, and it can be envisaged that sections of the surface are not satisfactorily compensated due to the large variance in topography and shadowing of some areas (indicated by the positive signs). Note that on some XPS instruments,

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2019 The Authors Surface and Interface Analysis Published by John Wiley & Sons Ltd



**FIGURE 1** Charge neutralisation by electrons on A, “flat” and B, “rough” surfaces

the use of magnetic confinement systems can greatly improve the trajectory of electrons and send them spiralling towards the surface, which sometimes aids compensation in this type of sample.<sup>3</sup>

To overcome such topographical difficulties, some XPS instruments are configured with “dual-beam flood sources,” which use a combination of low energy electrons and argon ions, where the energy of the ions is expected to be below that required for bond breaking.<sup>4</sup> The use of argon as a neutralising agent has been used previously in both SIMS and AES communities<sup>5,6</sup> and is employed to eliminate charges on the sample surface in unilluminated area surrounding the X-ray footprint, aiding the neutralisation of the illuminated region with the low energy electrons. Indeed, even for an XPS system configured with an electron-only flood source, one of the present authors has often used back-filling of the analysis chamber with a low pressure of argon to aid charge neutralisation for particularly rough samples.

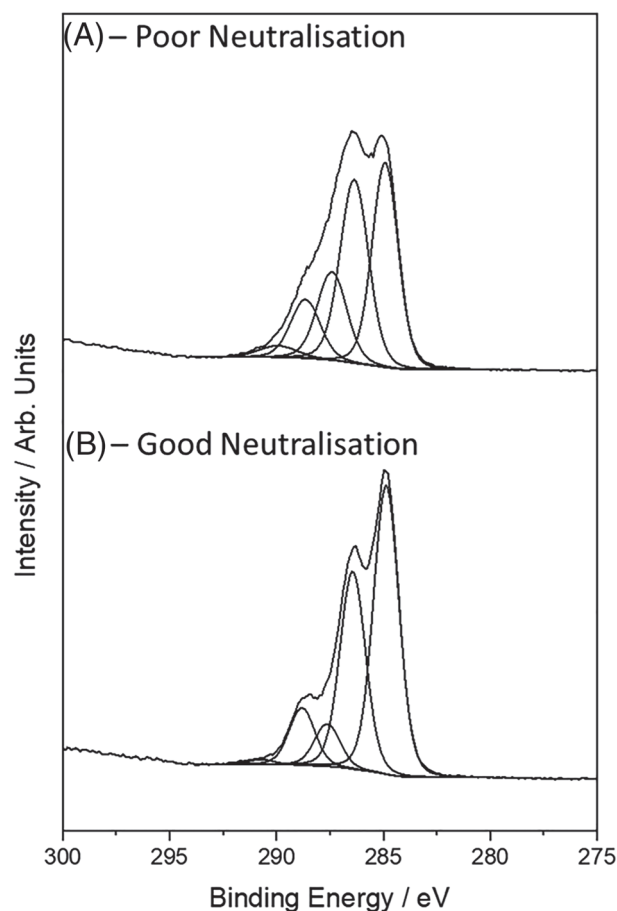
An example of the effectiveness of different charge compensation methods for rough surfaces is shown in Figure 2, which shows the C(1s) core-level spectra for a section of fabric which has a very random fibrous texture. For the dual flood source, the C(1s) spectra (Figure 2A) reveal carbon chemistry similar to that expected based on the parent chemical structure, whereas for electron only charge compensation from a second system with electron only compensation, the random orientation of the fibres results in a less defined C(1s) envelope, the chemistry of which could readily be misinterpreted.

## 2 | INTRODUCTION: SCOPE OF THIS WORK

Typically, dual-mode sources are designed to be turn-key solutions where one mode is suitable for many sample types. However, Steinberger et al have previously reported<sup>7</sup> that on a system where both dual-mode and electron only compensation were available, some care should be taken in the selection of charge compensation conditions. In their study of chromium (VI) compounds, during XPS analyses with different charge compensation modes, they observed different rates of Cr(VI) reduction, concluding that low energy ions from dual flood guns actually accelerate reduction of these compounds. Ultimately, they concluded that chromium samples prone to such reduction should be analysed using an electron flood source only and preferably with additional cooling. Of course, reduction of metal ions during XPS analysis is not uncommon

and has been observed on a variety of XPS systems, with the reduction of Au (III),<sup>8,9</sup> Pd(II),<sup>10</sup> Cu(II),<sup>10-12</sup> Hg(II), Bi(III), and W(VI) reported<sup>9</sup>; additionally, potential reduction by the vacuum environment of the spectrometer or from neutralising electrons should not be neglected.<sup>7</sup>

From the point of view of the analyst, however, it is preferable to use the same turn-key dual-mode charge compensation source for all



**FIGURE 2** C(1s) spectra for a rough fabric surface, where the spectra are recorded with A, an electron only neutralisation source and B, a dual neutralisation source. For clarity, the poorly neutralised spectrum was charge referenced to spectrum (B) and fitted with a similar peak profile to that of the well-neutralised spectrum to illustrate the erroneous chemistry that may be inferred

samples, without having to resort to extra sample treatments. In the remainder of this paper, we present a recently developed dual mode charge compensation method which has been shown to compensate Cr(VI) oxide without any significant reduction, even when prolonged sample analysis times are required. This enables the user to retain the previously explained benefits of combined electron/argon ion compensation during conventional XPS analysis, whilst maintaining the chemical integrity of their samples.

### 3 | EXPERIMENTAL

All analysis was performed on Thermo Scientific Nexsa or K-Alpha<sup>+</sup> XPS systems, both equipped with a monochromatic Al-K $\alpha$  source operating at a power of 72 W (6 mA  $\times$  12 kV). The X-rays are microfocused, with a source-defined elliptical analysis area of ca. 400  $\mu$ m  $\times$  800  $\mu$ m and termed the 400- $\mu$ m spot. Although the spot size is tuneable from 400  $\mu$ m to a minimum of 10  $\mu$ m, we have not extensively studied the influence this may have on the neutralisation; however, some initial experiments at half the spot size used herein does not seem to alter our findings.

Each system was equipped with the same standard design of dual-mode flood source for charge compensation (see Figure 3), where both electrons and argon ions are generated within the same source. Spectra are presented as recorded, where the C(1s) line for adventitious carbon is found at 284.8 eV.

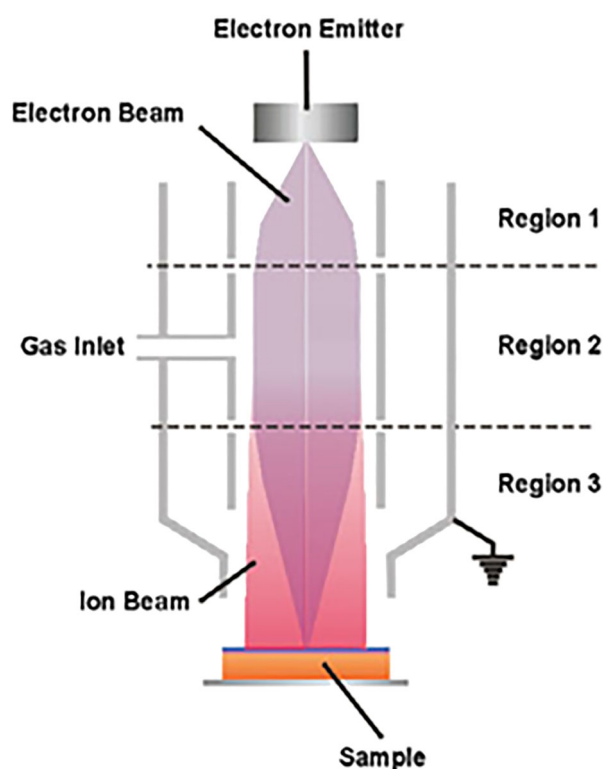
In the dual-mode flood source, with reference to Figure 3, electrons are emitted and accelerated in Region 1, before colliding with argon

admitted through a gas inlet tube in Region 2. This creates the argon ions, which are then accelerated with the electrons towards Region 3, where both beams are then focussed onto the sample surface.

With this type of combination source, if the flux of electrons is varied, then the flux of ions will also be affected. Additionally, by adjusting the various electrical potentials in Regions 1 to 3, it is also possible to differentially adjust the relative amounts of electrons and argon ions in the final combined beam for compensation. It is this latter approach which was used in this work to create two flood gun settings, referred to *Flood Gun Setting A* and *Flood Gun Setting B* for the remainder of this work.

Under both settings, the electron emission current for the dual neutraliser was 100  $\mu$ A. This parameter sets the flux of electrons generated. The difference between the two settings is related to the extractor voltage which varies the accelerating potential experienced by the electrons before collision with the argon to generate ions. Under Flood Gun Setting B, the electrons' impact potential was reduced by 10 V compared with Setting A. The effect of this voltage change is to reduce the cross section for ionisation of the argon atoms, effectively changing the balance of electrons and argon ions in the combined charge compensation beam. As the set-up routine of many charge compensation systems is based on the C(1s) spectra for polyethylene terephthalate (PET), the results of both flood gun modes on the PET spectra are presented in the ESI (Figure S1), with both spectra exhibiting negligible difference, and highlight the stability and versatility of the source under different operating conditions.

Unless otherwise stated, all XPS data were acquired in a total time frame of ca. 60 minutes, which is not unrealistic of many acquisition time scales in XPS analysis. All samples used in the study were purchased from their respective manufacturer and used without further treatment. All powders were gently pressed into the wells of a Thermo Scientific powder holder plate, whilst flake-like materials were held with a small section of a double-sided carbon tape.



**FIGURE 3** Schematic showing the combined dual-mode charge compensation flood source used in this work

## 4 | RESULTS

### 4.1 | Cr (VI) species

It was prudent to investigate some of the compounds studied by Steinberger<sup>7</sup> as a starting point. With this, we chose to study potassium chromate (K<sub>2</sub>CrO<sub>4</sub>, Alfa Aesar, 98%), sodium dichromate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O, Alfa Aesar, 99%), and chromium (VI) oxide (CrO<sub>3</sub>, Alfa Aesar, 99%). Due to the high oxidising potential of CrO<sub>3</sub>, we chose to study flakes of the material as opposed to a powder on safety grounds and ease of handling. Note the flakes themselves were not homogeneous and, even before prolonged analysis, showed variability in the initial concentration of reduced Cr states, the presence of which have been typically attributed to reaction with water vapour, hydrocarbons, or hydrogen.<sup>7,13</sup> With this in mind, the concentration of these reduced states however does not affect the observations pertinent to this study. Furthermore, it is important to stress that we note there is negligible influence from the X-rays in

the reduction of Cr(VI). Experiments where an area of a  $\text{CrO}_3$  flake was analysed in *ca.* 30 seconds using dual neutralisation and then exposed to only X-rays for 60 minutes before being reanalysed indicated no significant change to the Cr2p spectra (ESI, Figure S2).

When exposing a  $\text{CrO}_3$  sample to a dual-beam flood source, Steinberger et al<sup>7</sup> reported that the relative Cr(VI):Cr(III) concentration changed from 80:20 to *ca.* 50:50 in only 60 minutes. They also reported the rate of this reduction can be minimised by precooling the sample below  $-100^\circ\text{C}$ . However, cooling of samples is typically cumbersome and prone to condensation of contaminants from the vacuum and not available on all XPS systems, so ideally another solution is preferred.

Using our two different flood gun settings, we were able to emulate the work of Steinberger et al and observe a reduction of Cr(VI) to Cr(III) in a comparable time timescale (Figure 4A). With the second set of conditions, it was possible to virtually eliminate any observable damage to the Cr(VI) chemical state (Figure 4B), even without cooling.

Similarly, as shown in Figure 5, analysis of both chromate and dichromate salts investigated yielded similar increased stability during analysis, although as noted in the previous work, reduction of the dichromate is greater than the chromate.<sup>7</sup>

## 4.2 | V(V) species

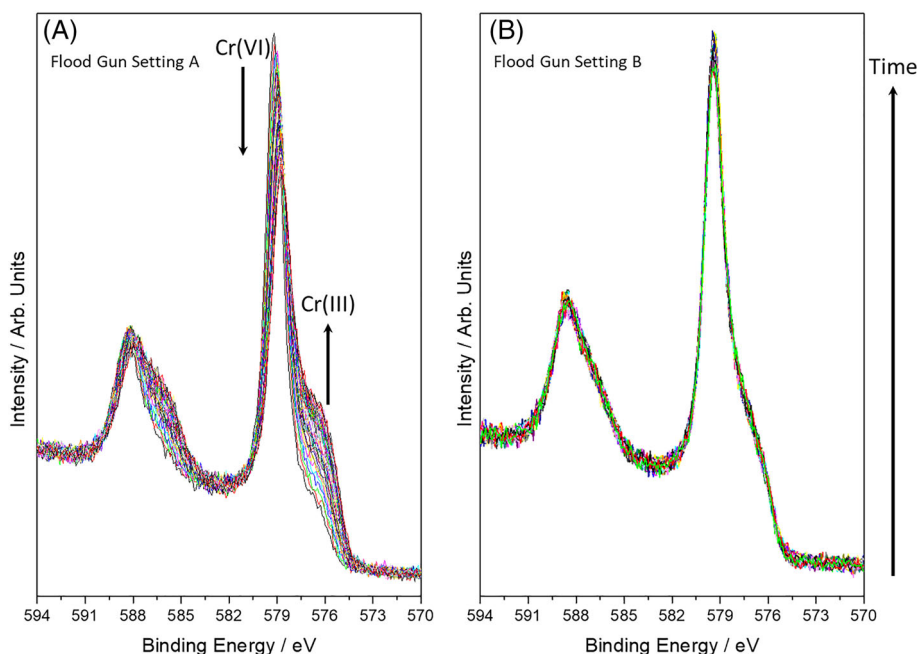
To further evaluate the difference between two charge compensation modes, the catalytically important material vanadium pentoxide,  $\text{V}_2\text{O}_5$ ,<sup>14</sup> was analysed because it is known to undergo reduction during XPS analysis.<sup>15,16</sup> Although bulk  $\text{V}_2\text{O}_5$  (Sigma Aldrich, 99.99%) was studied, the potential for increased reduction rates during analysis for nanoparticulate systems should be appreciated.<sup>17</sup>

Figure 6 shows the results from the analysis of a bulk  $\text{V}_2\text{O}_5$  powder. For higher emission currents (Figure 6A), there is a systematic increase of reduced vanadium states as a function of analysis time; the change in peak areas obtained by a simple Gaussian fit composed of two components is shown graphically in Figure 7. The gradual downward shift in energy (*ca.*  $-0.4$  eV) of both O(1s) and V(2p) peaks in Figure 6A is a consequence of the reduction and attributed to the lower concentration of equivalent V-O sites. Full V(2p)/O(1s) spectra are shown in the ESI, Figure S3.

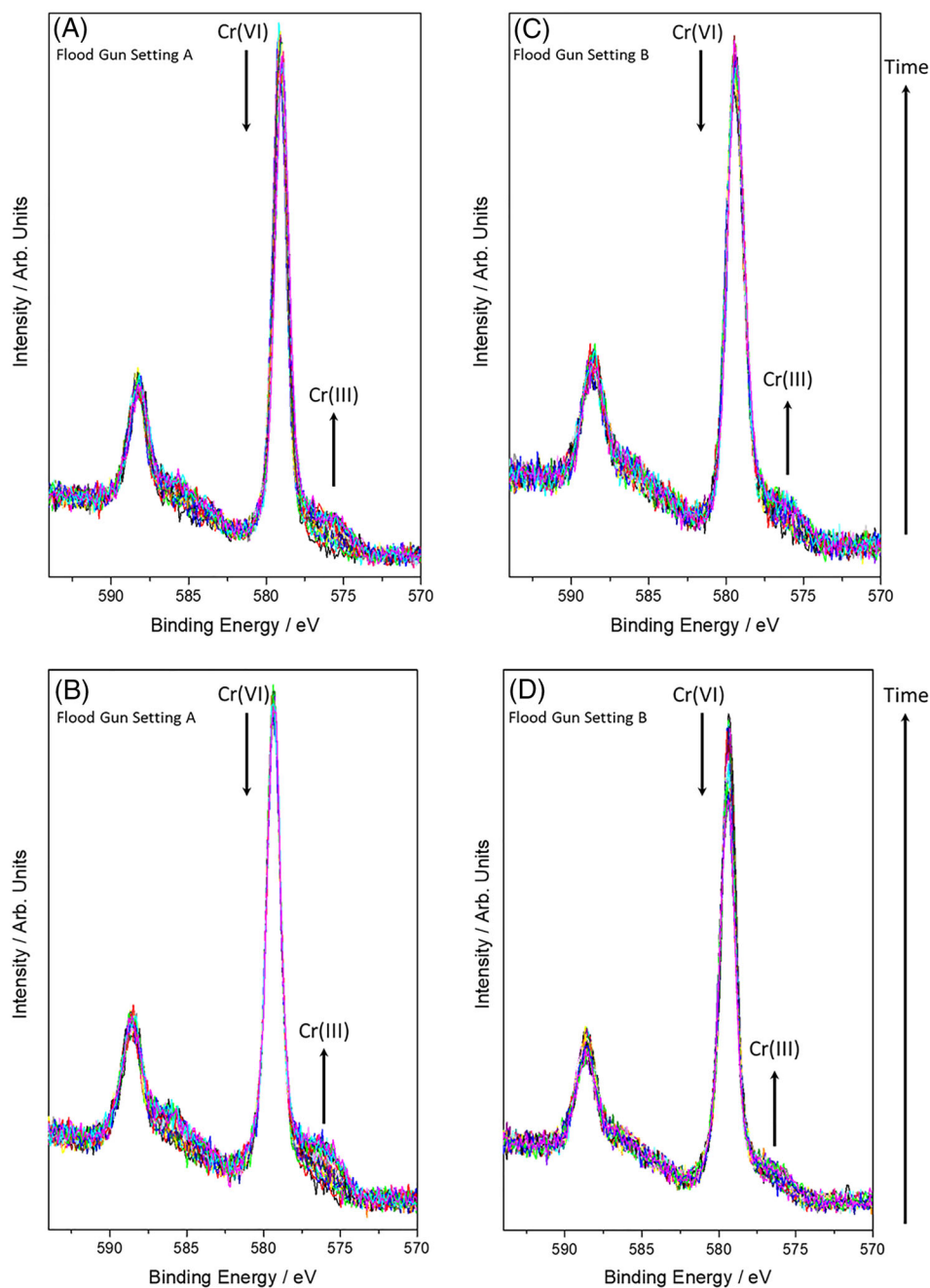
As observed for the Cr(VI) compounds, changing from flood gun setting A to setting B almost eliminates reduction of the V(V) state. For flood gun setting A, a clear increase in the amount of reduced vanadium states is observed as a function of time over the 60-minute analysis, whereas switching to flood gun setting B, only a very slight change in the ratio of vanadium states was observed after an equivalent exposure time as shown graphically in Figure 7.

## 4.3 | Cu(II) species

Reduction of Cu(II) species during XPS analysis is well known<sup>11,12</sup> with researchers taking different steps including cryogenic temperatures,<sup>18</sup> application of a bias<sup>19</sup> and rapid, multiple point acquisitions<sup>20</sup> to minimise it. Controlling the reduction of Cu(II) during XPS analysis is especially important in the study of metal-organic frameworks (MOFs),<sup>21</sup> which are porous networks formed by bonds between organic linkers and metal ions. The growth in studying their surface chemistry is driven by their promise in areas such as energy storage, heterogeneous catalysis, and sensing applications.<sup>22-24</sup>



**FIGURE 4** Overlaid Cr(2p<sub>3/2</sub>) core-level spectra for  $\text{CrO}_3$  where A, flood gun setting A and B, flood gun setting B, clearly illustrating the advantages of setting B inhibiting reduction



**FIGURE 5** Overlaid Cr(2p) core-level spectra acquired over a time frame of *ca.* 60 minutes, where A,  $K_2CrO_4$ ; B,  $Na_2Cr_2O_7 \cdot 2H_2O$  acquired under flood gun settings A; and C,  $K_2CrO_4$ ; D,  $Na_2Cr_2O_7 \cdot 2H_2O$  acquired under flood gun setting B. The improvements in reduction during analysis using setting B are clearly evident

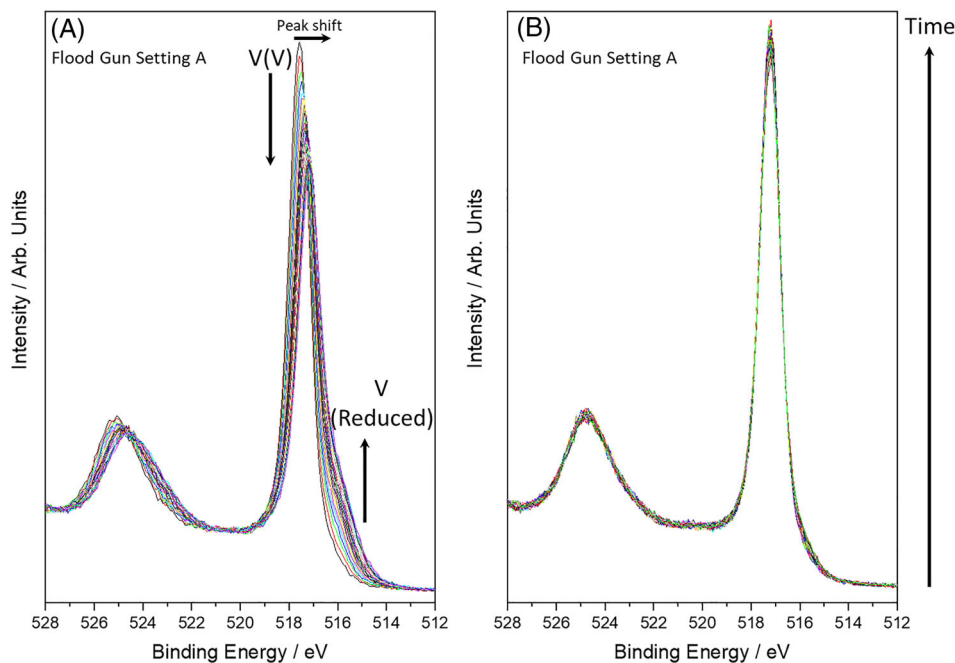
To study the effect of the neutraliser on these copper species, we have investigated the NOTT-100 MOF, which is often used for hydrogen adsorption; the MOF itself is composed of a Cu(II) centre, linked by H4BPTC (biphenyl-3,3',5,5'-tetracarboxylic acid) moieties.<sup>25</sup>

Figure 8 clearly shows reduction of the Cu(II) for flood gun setting A, whilst for lower emission currents, the reduction is almost eliminated, enabling acquisition of a close to pristine Cu(2p<sub>3/2</sub>) spectrum for such materials analysed with dual neutralisers. It is of note that although we have assigned the reduced state as Cu(0), without analysis of the Cu Auger signal, this could equally be Cu(I).

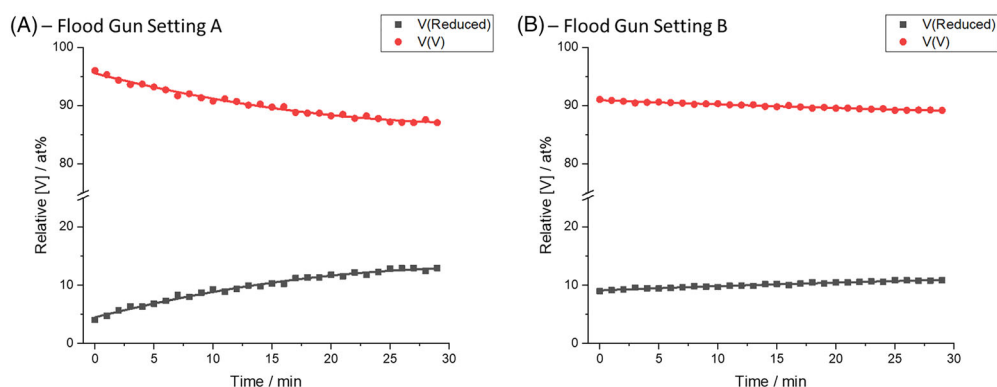
## 5 | MECHANISM OF REDUCTION

Based on the data recorded in this study, reduction can be correlated with loss of carbon from the surface, an observation which is diametrically opposed to that of Steinberger et al who concluded that accumulated hydrocarbons did not play a significant role.<sup>7</sup>

To illustrate this, we shall consider the case of  $CrO_3$ , and whilst it is acknowledged that  $V_2O_5$  exhibits a loss of surface carbon,  $CrO_3$  is used as an exemplar due to the greater overall degree of reduction. Here, a clear difference in the C(1s) concentration between the two



**FIGURE 6** V(2p) core-level spectra for  $V_2O_5$ , where: A, overlay of spectra acquired with flood gun setting A and B, overlay of spectra acquired with flood gun setting B clearly showing that setting A reduces  $V_2O_5$  more readily than setting B



**FIGURE 7** V(V) and reduced state relative concentrations fitted from the  $V2p_{3/2}$  spectra for a  $V_2O_5$  powder sample, where: A, spectra were acquired with flood gun setting A and B, spectra were acquired with flood gun setting B. Note the oxide already contained some reduced states in the region of ca. 5% to 8% of the total vanadium content

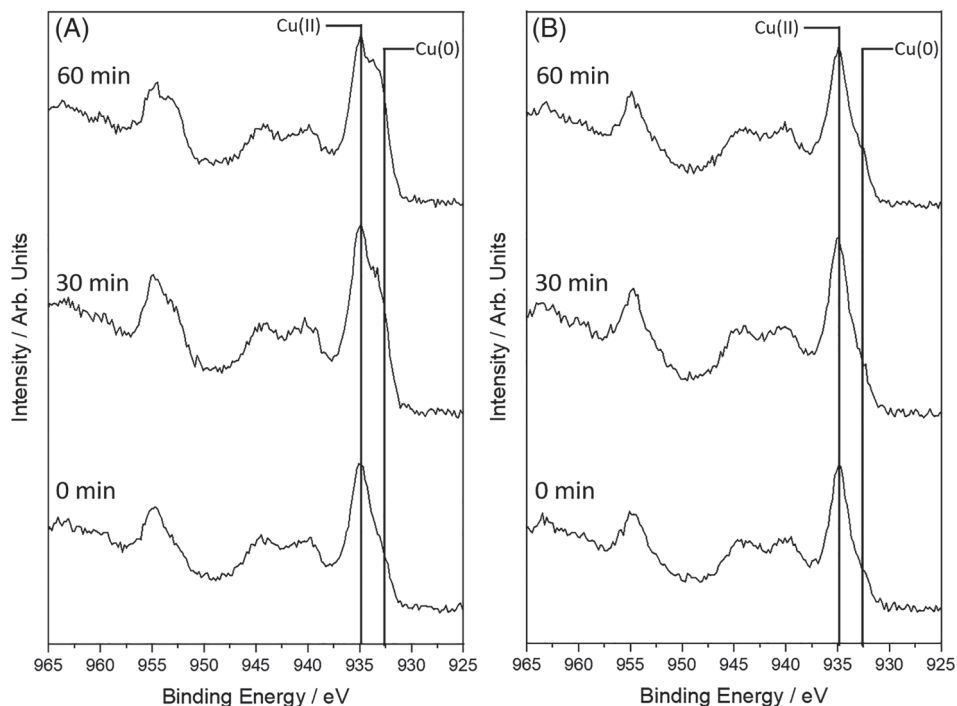
flood gun modes employed can be seen (Figure 9). Replicating the experiments of Steinberger,<sup>7</sup> where the sample is subjected solely to prolonged neutraliser exposure, we observe negligible difference in the carbon concentration for the optimised flood gun settings, whereas the original settings exhibit a significant carbon loss as indicated the carbon atomic percentage ( $\sigma_c$ ) and the overall spectral noise over a 30-minute period. An example of a typical iterative experiments where the carbon is recorded along with chromium and oxygen over a period of 60 min is given in the ESI, Figure S4.

The loss is predominantly the aliphatic, or  $sp^3$ -like carbon state at ca. 285 eV. As already highlighted, there is minimal influence from the monochromatic X-rays which further exemplifies that reduction is down to the dual ion source and the impact energy is critical in controlling any change in the surface chemistry.

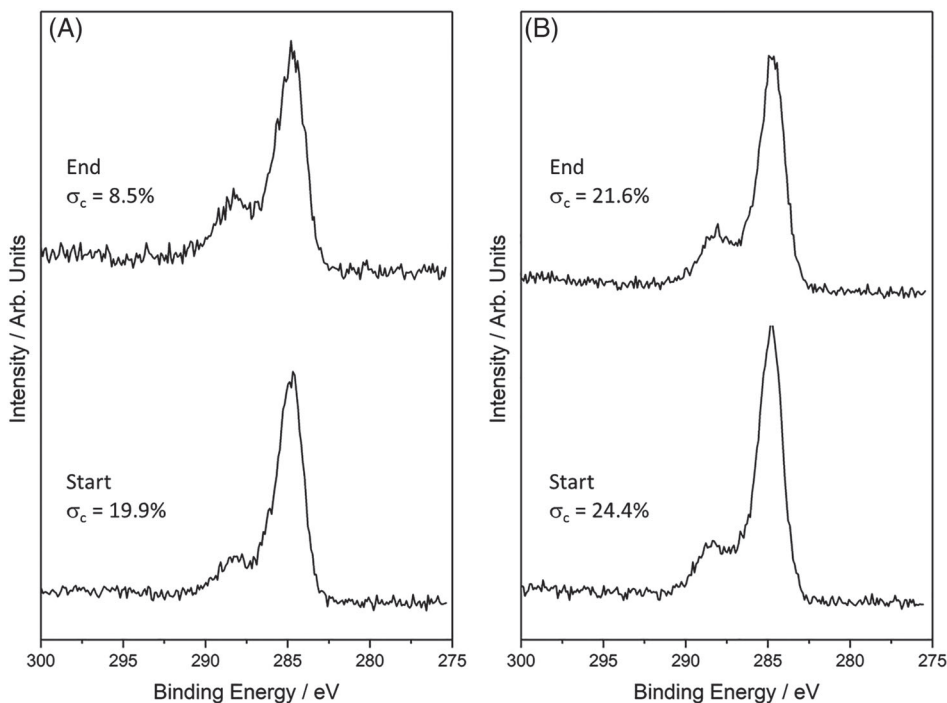
Whilst the decrease of carbon does not discount any other specific reduction mechanisms, such as “colombic explosion” releasing both charged and neutral species by means of Auger decay,<sup>26</sup> the loss of carbon from the surface is likely to be as CO containing species ultimately reducing the surface. Regardless of the reduction mechanism, the very nature of the spectrometers employed precludes addition of a gas analyser for mass spectroscopic analysis of desorption products<sup>27</sup>; however, the authors note that more configurable XPS systems equipped with similar charge compensation sources may facilitate such a study.

Whilst we can correlate reduction of the metal oxides with a loss of carbon, this is not true for the NOTT-100 MOF wherein no discernible difference is observed in the C(1s) core-level spectra (ESI, Figure S5). Whilst Cu (II) can reduce under prolonged X-ray exposure,





**FIGURE 8** Cu(2p) spectra for A, flood gun setting A and B, flood gun setting B, taken at 30 minutes intervals; flood gun setting B clearly minimises the extent of reduction



**FIGURE 9** C(1s) spectra and total carbon concentration ( $\sigma_c$ ) for the adventitious carbon on  $\text{CrO}_3$  flakes for A, flood gun setting A; B, flood gun setting B taken at the start and end of a 30-minute analysis. Clearly, setting B has a negligible influence on the carbon content

typically believed to be due to secondary electron emission,<sup>19</sup> the use of the optimised flood gun settings indicates we can mitigate reduction regardless of continued X-ray exposure. Therefore, it is possible

the observed reduction either results from ion-induced secondary electron emission<sup>28</sup> or via an Auger decay mechanism of the copper centre<sup>26,29</sup> as proposed for the metal oxides.

## 6 | CONCLUSIONS

The instruments used in this study are high-performance, turn-key systems and designed for rapid acquisition of high-quality data. Most data acquisition can be completed within minutes or a few tens of minutes, but where longer experimental times are required, if dual flood source conditions similar to those of Steinberger et al.<sup>7</sup> are used, then the surface chemistry of some multivalence transition metal compounds may be modified in a manner which can be correlated with the removal of surface carbon.

A simple change in the dual source operating parameters, however, can dramatically minimise or even eliminate the observed reduction, even for XPS acquisition times up to 1 hour. Under these conditions, the benefits of dual source charge compensation are available (allowing high quality analysis of rough polymers, for example) with little to no negative effect on the surface chemistry of the sample.

For the materials discussed, we have demonstrated that this simple change can greatly reduce and, in some cases, eliminate reduction during analysis. However, where there is potential for any surface chemical reduction, the careful experimentalist can acquire the high valency spectral regions of interest first in the experiment and then again at the end to confirm that there is little or no modification. Indeed, it is highly recommended that where possible samples with elements known to potentially reduce are prescreened by means of a sacrificial sample and, where appropriate, modification of the flood gun settings are made. Based on our findings, using flood gun setting B, a reduction of 5% or less is comfortably achieved within 60 minutes.

For users uncomfortable, or unable to change analysis conditions, then it is recommended that for using flood gun settings A, a protocol similar to that below is adopted:

- Total analysis time is kept under 10 minutes per sample (or analysis area) to keep the level of potential reduction below ca. 10%
- Elemental regions susceptible to reduction, such as Cr(2p), are recorded as the first and last regions together with the C(1s) core level to ascertain any levels of reduction and possible cause

In the future, it would be useful to extend this work to other metal oxides and other compound types to confirm that the modified dual source flood mode continues to operate successfully with little or no sample modification.

## ACKNOWLEDGEMENTS

Part of this work was performed at the Engineering and Physical Sciences Research Council (EPSRC) National Facility for XPS ("HarwellXPS"), operated by Cardiff University and UCL, under EPSRC contract No. PR16195. LE thanks Cogent Power Ltd (Newport) for sponsorship. D.J.M. is grateful to Alex Tansell of Dr Timothy L. Easun's group at Cardiff University for the MOF sample. Information on the data underpinning the results presented here, including how to access them, can be found in the Cardiff University data catalogue at <http://doi.org/10.17035/d.2019.0069433902>.

## ORCID

David J. Morgan  <https://orcid.org/0000-0002-6571-5731>

## REFERENCES

1. Briggs D, Grant J (Eds). *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*. Chichester: IM Publications; 2003.
2. Barth G, Linder R, Bryson C. Advances in charge neutralization for XPS measurements of nonconducting materials. *Surf Interface Anal*. 1988;11(6-7):307-311.
3. Walker A. Vol. US Patent: 4810879, 1989.
4. Larson PE, Kelly MA. Surface charge neutralization of insulating samples in x-ray photoemission spectroscopy. *J Vac Sci Technol A*. 1998;16(6):3483-3489.
5. Hunt CP, Stoddart CTH, Seah MP. The surface analysis of insulators by SIMS: charge neutralization and stabilization of the surface potential. *Surf Interface Anal*. 1981;3(4):157-160.
6. Wolstenholme J. *Auger Electron Spectroscopy: Practical Application to Materials Analysis and Characterization of Surfaces, Interfaces and Thin Films*. New York: Momentum Press; 2015.
7. Steinberger R, Duchoslav J, Greunz T, Arndt M, Stifter D. Investigation of the chemical stability of different Cr(VI) based compounds during regular X-ray photoelectron spectroscopy measurements. *Corros Sci*. 2015;90:562-571.
8. Fong YY, Visser BR, Gascooke JR, et al. Photoreduction kinetics of sodium tetrachloroaurate under synchrotron soft X-ray exposure. *Langmuir*. 2011;27(13):8099-8104.
9. Süzer Ş. XPS investigation of X-ray-induced reduction of metal ions. *Appl Spectrosc*. 2000;54(11):1716-1718.
10. Fleisch TH, Zajac GW, Schreiner JO, Mains GJ. An XPS study of the UV photoreduction of transition and noble metal oxides. *Appl Surf Sci*. 1986;26(4):488-497.
11. Di Castro V, Piredda G. Photoinduced reduction of silica supported CuO during XPS irradiation. *Chemical Physics Letters*. 1985;114(1):109-113.
12. Poulston S, Parlett PM, Stone P, Bowker M. Surface oxidation and reduction of CuO and Cu<sub>2</sub>O studied using XPS and XAES. *Surf Interface Anal*. 1996;24(12):811-820.
13. Kagwade SV, Clayton CR, Halada GP. Causes and prevention of photochemical reduction of hexavalent chromium during x-ray photoelectron spectroscopy. *Surf Interface Anal*. 2001;31(6):442-447.
14. Wachs IE. Catalysis science of supported vanadium oxide catalysts. *Dalton Trans*. 2013;42(33):11762.
15. Knotek ML, Feibelman PJ. Stability of ionically bonded surfaces in ionizing environments. *Surf Sci*. 1979;90(1):78-90.
16. Silversmit G, Depla D, Poelman H, Marin GB, De Gryse R. An XPS study on the surface reduction of V<sub>2</sub>O<sub>5</sub>(001) induced by Ar<sup>+</sup> ion bombardment. *Surf Sci*. 2006;600(17):3512-3517.
17. Baer DR, Engelhard MH, Johnson GE, et al. Surface characterization of nanomaterials and nanoparticles: important needs and challenging opportunities. *J Vac Sci Technol A*. 2013;31(5):50820.
18. Pantano C, D'Souza A, Then A. In: Czanderna A, Powell C, Madey T, eds. *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*. New York: Plenum Press; 1998:39.
19. Iijima Y, Niimura N, Hiraoka K. Prevention of the reduction of CuO during X-ray photoelectron spectroscopy analysis. *Surf Interface Anal*. 1996;24(3):193-197.
20. Cros A. Charging effects in X-ray photoelectron spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena*. 1992;59(1):1-14.



21. Duke AS, Dolgoplova EA, Galhenage RP, et al. Active sites in copper-based metal-organic frameworks: understanding substrate dynamics, redox processes, and valence-band structure. *J Phys Chem C*. 2015; 119(49):27457-27466.
22. Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT. Metal-organic framework materials as catalysts. *Chem Soc Rev*. 2009; 38(5):1450-1459.
23. Silva P, Vilela SM, Tome JP, Almeida Paz FA. Multifunctional metal-organic frameworks: from academia to industrial applications. *Chem Soc Rev*. 2015;44(19):6774-6803.
24. Wang H, Zhu Q-L, Zou R, Xu Q. Metal-organic frameworks for energy applications. *Chem*. 2017;2(1):52-80.
25. Lin X, Telepeni I, Blake AJ, et al. High capacity hydrogen adsorption in Cu(II) tetracarboxylate framework materials: the role of pore size, ligand functionalization, and exposed metal sites. *J Am Chem Soc*. 2009;131(6):2159-2171.
26. Ramsier RD, Yates JT. Electron-stimulated desorption: principles and applications. *Surf Sci Rep*. 1991;12(6-8):246-378.
27. Massey S, Alizadeh E, Rowntree PA, Sanche L. On the possibility of using low-energy electron stimulated desorption of ions as a surface probe: Analysis of Au substrates. *Int J Mass Spectrom*. 2016;394:330.
28. Walton SG, Tucek JC, Champion RL. Low energy, ion-induced electron and ion emission from stainless steel: the effect of oxygen coverage and the implications for discharge modeling. *J Appl Phys*. 1999;85(3):1832-1837.
29. Knotek ML, Feibelman PJ. Ion desorption by core-hole Auger decay. *Phys Rev Lett*. 1978;40(14):964-967.

## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**How to cite this article:** Edwards L, Mack P, Morgan DJ. Recent advances in dual mode charge compensation for XPS analysis. *Surf Interface Anal*. 2019;51:925-933. <https://doi.org/10.1002/sia.6680>