ESRF	**Experiment title:** **High energy photoemission study of the electronic structure of β-PbO_2**	**Experiment number**: HE-2138
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Report:

Lead dioxide (PbO_2) is of ubiquitous importance as the medium for storage of chemical energy on the cathode plate in lead acid batteries and is therefore a material of immense technological importance. However it's electronic properties have been little studied. It is not always recognised that PbO_2 is in fact a *metallic* conductor, but the ability of lead acid batteries to deliver the high currents necessary to drive the starter motor for an internal combustion engine is crucially dependent on the low resistance of the cathode coating. The reason *why* PbO_2 is metallic has provoked ongoing controversy in two ways. Firstly, bandstructure calculations have suggested that the metallic behaviour is an intrinsic property of stoichiometric β-PbO_2 due to overlap of the Pb 6s conduction band with the valence band of O 2p states [1]. However, we recently reported Al Kα valence band X-ray photoelectron spectra of β-PbO_2, which in combination with density functional calculations, demonstrated unambiguously that metallic behaviour arises from population of electronic states *above* the top of the main O 2p valence band [2]. These carriers must be introduced by oxygen vacancy defects so that the oxide should be formulated as PbO_{2-x}. The composition parameter is variable but assumes a value x=0.042 after annealing in UHV at 230°C for 1 hour. This gives a dilute but degenerate gas of conduction electrons with a carrier concentration of 2×10^{21} cm^{-3}. Lower carrier concentrations of around 1×10^{21} cm^{-3} are found for un-annealed samples. The associated conduction electron plasmon energies fall in the range between 0.7 eV and 1.0 eV. Secondly there is no consensus on the detailed atomic make up of the conduction band states. The textbook view is that the *empty* conduction band is of predominant Pb 6s atomic character. However we recently carried out O K shell X-ray emission (XES) measurements on PbO_2 [3]. These reveal that a filled valence band state 9 eV below the Fermi energy in fact has only minority O 2p character and by default it can be inferred that it has *majority* Pb 6s character. Thus conduction band states must be dominantly O 2p like. It is however impossible to confirm the atomic nature of states at the bottom of the valence band directly by Pb 4p or Pb 5p XES as both these core levels suffer lifetime broadening in excess of 6 eV, rendering the emission spectra featureless.

The screening response of the conduction electrons in PbO_{2-x} has a profound influence on the structure of core photoemission lines. As shown in figure 1, the Pb 4f$_{7/2}$ core line excited at 1486.6 eV consists of a pair of a sharp and weak component at low binding energy and broader and stronger Lorentzian "satellites" at higher binding energy. In terms of the model introduced by Kotani [4], the low binding energy peaks corresponds to a “well screened” final state whereas the high binding energy “satellites” correspond to “unscreened” final states. However that the separation between the peaks is close to the conduction electron plasmon energy and increases with increasing carrier concentration in parallel with the plasmon energy, so we could alternatively describe the high binding energy peaks as unusually strong plasmon satellites [5, 6]. This interpretation of the Pb 4f core lineshape in terms of final state effects that are an intrinsic property of PbO_2 is however controversial: in previous XPS work [e.g. 7] it had always been assumed that the complex core lineshape is associated with ill-defined “surface phases” with multiple oxidation states.

The two main objectives of experiment HE-2138 conducted on beamline ID16 on the ESRF using the hard XPS “VOLPE” endstation were therefore as follows:

(a) to identify the distribution of Pb 6s states within the valence and conduction bands by exploitation of the fact that the cross section for ionisation of Pb 6s states had been calculated to increase dramatically relative to that of O 2p states on increasing the photon energy from 1486.6 eV to 6000 eV or higher [8].
(b) to establish that the complex Pb 4f core line shape is an intrinsic propert of bulk PbO_{2-x} and is not the result of “surface phases”. This aspect of the experiment exploits the fact that the electron inelastic mean free path for shallow core electrons is very much greater at “hard” photon energies than at 1486.6 eV

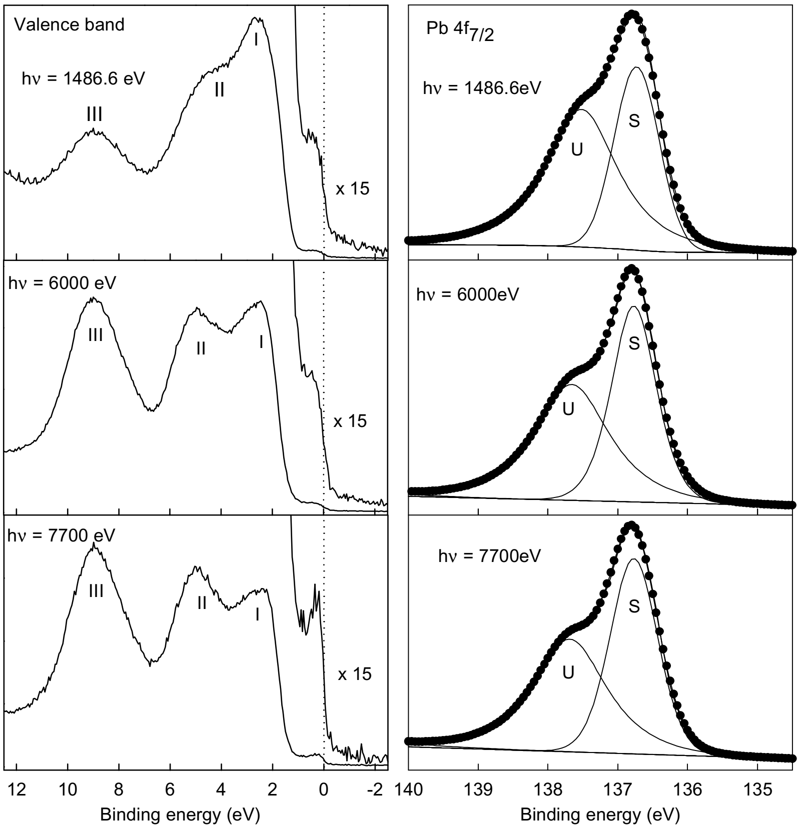

Figure 1.

Left hand panel: valence and conduction band photoemission of β-PbO_{2-x} excited at the photon energies indicated.

Right hand panel: Pb $4f_{7/2}$ XPS of β-PbO_{2-x} excited at the photon energies indicated. The spectral profiles have been fitted to two components due to screened (S) and unscreened (U) final states. Note the increase in the relative intensity of the screened component at high photon energy.

Valence and core level photoemission spectra of two samples of thick film β-PbO_2 were measured at photon energies of 6000 eV and 7700 eV, as shown in figure 1. The overall (beamline plus spectrometer) resolution was 360 meV at hν= 6000 eV and 250 meV at hν=7700 eV – values comparable with an overall resolution of 350 meV employed in our earlier XPS investigations [2] using a state-of-the-art offline XPS system incoporating a monochromated rotating anode X-ray source and a 300 mm mean diameter spherical sector analyser with parallel electron detection system. As can be seen in the figure the overall signal to noise in the high energy data is comparable with that obtained at hν=1486.6 eV even though ionisation cross sections are in absolute terms around 2 orders of magnitude lower for both O 2p and Pb 4f states at hν=7700 eV as compared with hν=1486.6 eV.

The valence band spectra show a very striking increase in the intensity of the valence band peak (III) at highest binding energy as compared with the lower energy features I and II. This establishes in a positive way - rather than by default - that the states in band III do indeed have significant Pb 6s character. At the same time the conduction band states (terminating in a metallic Fermi edge) are similarly enhanced showing that these states also have significant Pb 6s character. However the intensity of the valence band peak III increases by about a factor of two relative to the intensity of the Fermi edge emission on going from hν=1486.6 ev to hν=7700. This shows that there is more Pb 6s character in the lower valence bands states than in the conduction band. This conclusion is supported by the bandstructure calculations [2] but is at variance with the simplest ionic description which assumes that the conduction band states are of pure Pb 6s character.

Qualitatively the Pb 4f core lineshapes observed at high photon energies is very similar to that found at hν=1486.6 eV. This confirms the interpretation of the lineshape in terms of intrinsic final state screening processes. Quantitatively however the area ratio between "screened" and "unscreened" final state components increases from 0.70 at hν=1486.6 eV to 1.0 at hν=7700eV. Because the near-surface region contributes more strongly to the spectrum excited at 1486.6 eV, this suggests that core hole screening is suppressed in the near-surface region. This conclusion is in accord with recent experiments conducted on Spring-8 which show that core features due to coherent metallic screening in a number of systems including V_2O_3[9], $La_{1-x}Sr_xMnO_3$[10], $La_{0.85}Ba_{0.15}MnO_3$[11] and $Nd_{2-x}Ce_xCuO_4$[12] are very much stronger at 6 keV photon energy than in conventional XPS experiments, where the coherently screened structure is almost invisible. These materials are all highly correlated. The physics of this effect is far from clear but the present results demonstrate that the suppression of metallic screening in the near-surface region probed in conventional XPS is very much less pronounced in metallic PbO_{2-x} - which can be regarded as a dilute free-electron-like metal - than in the correlated metals discussed above.

In summary the Pb 6s contribution to valence and conduction band states in β-PbO_2 has been identified by hard X-ray photoemission spectroscopy. The strong enhancement in the intensity of metal-s derived states at high photon energies demonstrated in the present work should be of general value in the study of conduction bands in a large family of important transparent conducting oxide materials including Sn-doped In_2O_3 (ITO), Sb-doped SnO_2 and Al-doped ZnO. To date it has been exceedingly difficult to study the conduction band states in these materials by photoemission techniques due to the low cross section for ionisation of 4s or 5s states relative to O 2p states combined with the low carrier concentration and the interfering effects of surface states which fill much of the bulk bandgap [13,14]. The reduced surface sensitivity in hard XPS combined with the enhanced relative cross section for s states will faciliate a step-change in this area of applied spectrocopy and should enable resolution of a number of outstanding controversies [15], most notably the question as to whether the bandgap of In_2O_3 is direct or indirect [14,15].

A paper based on the current report has been submitted to Physical Review Letters [16].

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