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# Studies of the Thermal Decomposition of $\beta$NiO(OH) and Nickel Peroxide by X-ray Photoelectron Spectroscopy

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The thermal decomposition of both $\beta$NiO(OH) and 'nickel peroxide' have been studied by combining X-ray photoelectron spectroscopic (X.p.s.) studies of the solid with mass-spectrometric analysis of the gas phase. Through monitoring the O(1*s*) and Ni(2*p*) spectra of the as-prepared solids during decomposition, with simultaneous analysis of the gas phase, it has been established that 'nickel peroxide' behaves in an identical fashion to $\beta$NiO(OH). We conclude that the two solids are chemically identical; on the other hand previous studies of 'nickel peroxide' have suggested it to be a hydrated defective oxide $Ni_2O_3$. Central to our argument is the observation that both solids exhibit initially a single O(1*s*) peak at 530.5 eV, but during decomposition this peak splits into two components, one at 529.7 eV and the other at 531.4 eV. It is suggested that intercalated water within the $\beta$NiO(OH) structure results in the equivalence (by X.p.s.) of the 'oxygen species' through the stabilisation of 'OHO' groups. Water and molecular oxygen are the predominant gaseous decomposition products, the solid, at 773 K, being converted into defective NiO.

Photoelectron spectroscopy has revealed[1] interesting features in the interactions between oxygen and metallic nickel and also made possible distinctions between various defective forms of NiO. Differences in electronic states of both oxygen and nickel species, as well as evidence for surface hydroxyls and adsorbed water, have been documented, but nevertheless some disagreement as to the assignments of photoelectron peaks remains. It seemed likely that the higher oxides of nickel could prove a fruitful area of study, because the stoichiometry of some of these compounds suggests that the nickel exists in two oxidation states within the same compound and that oxygen is present in excess. Therefore evidence for changes in stoichiometry and oxidation states which would be anticipated to occur during thermal decomposition would be looked for in variations of the electron binding energies of the O(1*s*) and Ni(2*p*) spectra. The advantages of combining *in situ* X.p.s. with simultaneous monitoring of changes in the chemistry of the solid through mass-spectrometric analysis of the gas phase are obvious.

The higher oxides of nickel have resisted easy characterisation because some of their properties obscure results obtained by the usual techniques. For example, they are invariably hydrated which causes difficulties in X-ray diffraction measurements since the hydrated lattices exhibit shifted peak positions (usually attributed to disorder and particle-size effects) arising from occluded water molecules.[2] They are also highly oxidative, reacting with most support materials.

Nickel oxyhydroxide, one of the oxides studied here, is the oxidant in the nickel–cadmium battery reaction

$$2NiO(OH)+2H_2O+Cd \rightleftharpoons 2\,Ni(OH)_2+Cd(OH)_2.$$

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Both $Ni(OH)_2$ and NiO(OH) have the brucite structure, and upon electrolytic oxidation the crystal parameters change continuously from $a = 3.14$ Å and $c = 4.60$ Å for $Ni(OH)_2$ to $a = 2.82$ Å and $c = 4.85$ Å for NiO(OH). In the process, compounds of stoichiometry intermediate between $Ni(OH)_2$ and NiO(OH) such as $Ni_3O_2(OH)_4$ are observed.[3]

'Nickel peroxide', the other oxide studied in this investigation, is used as an oxidant in certain organic reactions but is, as yet, imperfectly characterised. Magnetic-susceptibility measurements of precipitates of a 'nickel peroxide' formed by continuous oxidation have been made[4] during the oxidation process, and these suggest the presence of $Ni^{III}$ and $Ni^{IV}$. The thermal decomposition of nickel peroxide has been investigated recently by Bond and Tripathi[5] using differential thermal analysis and thermal gravimetric analysis. The results suggested that the composition of nickel peroxide is probably best represented as $Ni_2O_3 \cdot 2H_2O$. Decomposition to NiO was shown to involve two endothermic processes at *ca.* 423 and 523 K, respectively. Mass-loss measurements were used to infer that the initial endothermic process involved loss of one mole of water per mole of $Ni_2O_3 \cdot 2H_2O$ followed by further dehydration and reduction to NiO *via* loss of both water and oxygen.[5]

The object of the present work is therefore two-fold: first to explore how X.p.s. can provide information relevant to the mechanism of the thermal decomposition of $\beta$NiO(OH) and secondly to examine the relationship, if any, between it and 'nickel peroxide'. We supplement the X.p.s. data, which provide spectroscopic information relevant to the outermost 20 Å or so of the solid, with a mass-spectrometric analysis of the gas phase, which reflects the chemistry occurring during the thermal decomposition of both the surface and bulk solid.

## EXPERIMENTAL

All spectra were taken using a VG ESCA-3 spectrometer.[6] The samples were finely ground powders which were pressed in a 13 mm die at 10 tonnes pressure into a square of fine stainless-steel mesh and then screwed onto the probe-end under a horseshoe-shaped gold clip, so that only the central portion of the sample was exposed to photons. The spectrometer and probe, without the sample, were previously baked at 453 K overnight, while filaments and gauges were degassed to $< 1 \times 10^{-9}$ Torr.* The sample was then mounted on the probe, admitted to the spectrometer under dry nitrogen and the spectrometer evacuated. A quadrupole mass spectrometer was used to monitor the evolution of gases from the sample during evacuation and heating while in the preparation chamber. Charging effects were small ($< 0.5$ eV), and binding energies are referenced to the graphite carbon C(1*s*) peak, which, when present, was observed at 284.9 eV. The concentration of the carbon was usually less than a tenth of that of the oxygen. The sample of $\beta$NiO(OH) was prepared by the usual method.[7] Nickel peroxide, supplied by B.D.H., was synthesized by persulphate oxidation of basic nickel salt solutions using the method of Nakagawa *et al.*[8]

## RESULTS AND DISCUSSION

### 1. DECOMPOSITION OF $\beta$NiO(OH)

Fig. 1 and 2 show the O(1*s*) and Ni($2p_{3/2}$) spectra of a sample of $\beta$NiO(OH) at various stages of thermal decomposition. Those designated (*a*) are for the sample before decomposition, but after the sample had been evacuated to $10^{-6}$ Torr at room temperature. The mass spectrum of the gas phase at this stage showed that the sample was evolving relatively large amounts of water vapour and some carbon dioxide

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* 1 Torr ≡ 101 325/760 Pa.

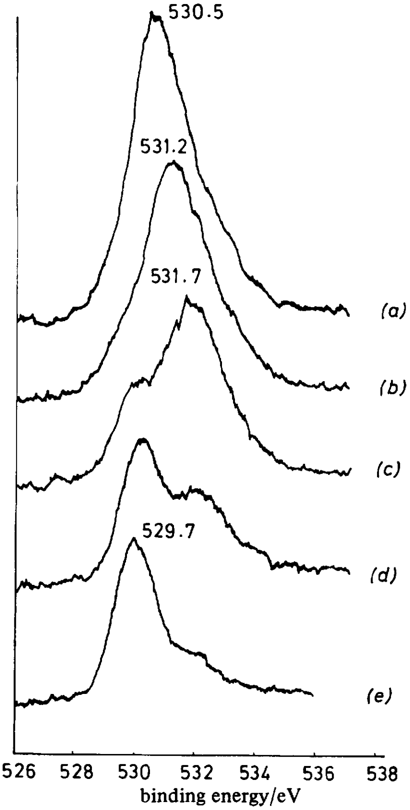

**Fig. 1.** O(1*s*) spectra for *β*NiO(OH) at 293 K at an ambient pressure of $5 \times 10^{-7}$ Torr (*a*), and during thermal decomposition for the following times: (*b*) 30 min, 423 K; (*c*) 30 min, 493 K; (*d*) 30 min, 623 K; (*e*) 4 h, 773 K. The total pressure increased to *ca.* $10^{-5}$ Torr at 623 K but decreased to $3 \times 10^{-7}$ Torr after 30 min at 773 K when oxygen and water evolution had become very slow. After cooling to 296 K spectrum (*e*) the sample was reheated *in situ* to 773 K. The pressure remained below $10^{-7}$ Torr and the O(1*s*) spectrum was identical to that shown in (*e*).

(40:1). The O(1*s*) profile initially exhibits a single symmetrical peak centred at 530.5 eV (f.w.h.m. = 2.4 eV), and the main Ni($2p_{3/2}$) peak is at 855.5 eV with its shake-up satellite 6 eV to higher binding energy. The sample was then heated to 423 K and held at that temperature for 30 min. Water vapour and to a lesser extent carbon dioxide (ratios ≈ 6:1) were evolved. The sample was recooled to room temperature and spectra (*b*) of fig. 1 and 2 obtained. The O(1*s*) profile shows that the single peak at 530.5 eV has been replaced by a peak at 531.2 eV with a shoulder at *ca.* 530 eV, while the Ni($2p_{3/2}$) peak has broadened slightly. The sample was heated again *in vacuo* to 493 K for 30 min. At temperatures above 423 K molecular oxygen was observed in the mass spectrum of the gas phase. At 493 K the low-binding-energy O(1*s*) peak at 529.7 eV is clearly resolved, but the peak at 531.7 eV still predominates [fig. 1(*c*)]. The Ni($2p_{3/2}$) spectrum [fig. 2(*c*)] mirrors to some extent the asymmetry to higher binding energies observed in the O(1*s*) profile. The same trend is seen in the spectra obtained after heating to 623 K. Oxygen evolution increased with respect to water, reaching a maximum of half the water concentration at 623 K. After this heating it can be seen [fig. 1(*d*)] that most of the oxygen in the sample is now in the form that gives rise

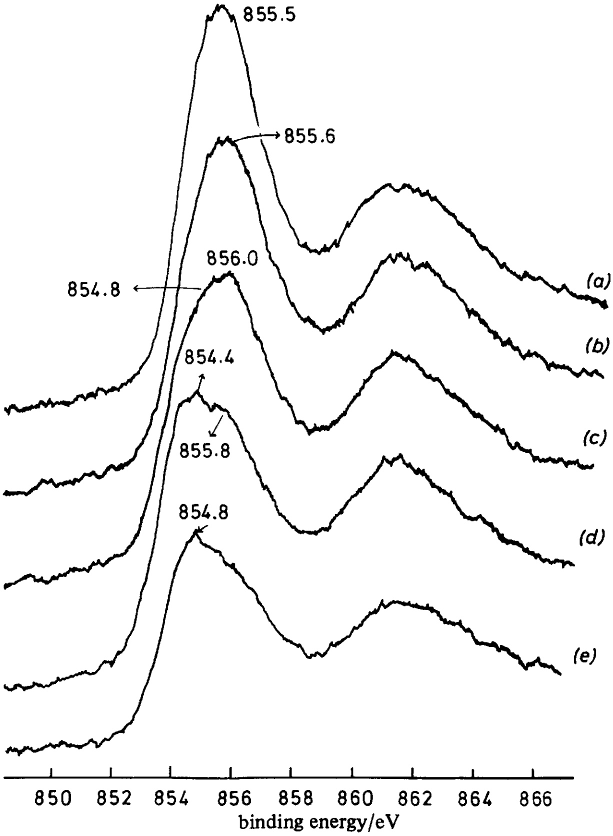

**Fig. 2.** Ni($2p_{3/2}$) spectra corresponding to O(1$s$) spectra shown in fig. 1.

to the O(1$s$) peak at 529.7 eV binding energy, while the 531.7 peak is the minor component. The Ni($1p_{3/2}$) peak also shows a shift with a low-binding-energy component predominating. The $\beta$NiO(OH) was finally heated to 773 K and held at that temperature for 4 h until the sample ceased evolving water or any other gas. The O(1$s$) spectrum [fig. 1 (*e*)] shows that only a small fraction of the high-binding-energy 531.4 eV O(1$s$) peak remains and the main Ni($2p_{3/2}$) peak is at 854.8 eV [fig. 2(*e*)].

Most of the spectra (fig. 1 and 2) show many similarities to those already observed for either nickel oxide or nickel hydroxide.[1] NiO typically has a low-binding-energy peak at 529.7 eV in the O(1$s$) spectrum and a peak at 854.0 eV in the Ni($2p_{3/2}$) spectrum which are associated with the $O^{2-}$–$Ni^{2+}$ interaction. Normally there are also peaks of lower intensity at a binding energy of 531.5 eV in the O(1$s$) spectral region and at *ca.* 856 eV in the Ni($2p_{3/2}$) region. These have been attributed to either a '$Ni_2O_3$ defect structure'[9] or to $O^-$ and $Ni^{3+}$ ion defects in the surface.[10–12]. $Ni(OH)_2$ also has a single O(1$s$) peak at 531.5 eV, which makes distinction between mixtures of $Ni(OH)_2$ and NiO difficult. The Ni($2p_{3/2}$) peak in $Ni(OH)_2$ occurs at *ca.* 856 eV.[13, 14]

Despite the information available to us from these previous studies, the single peak observed [fig. 1 (*a*)] in the initial O(1$s$) spectrum at 530.5 eV is not easy to understand. In particular it is intriguing to observe a single O(1$s$) peak when two peaks of equal intensity would clearly be expected for the oxide and hydroxide components [seen,

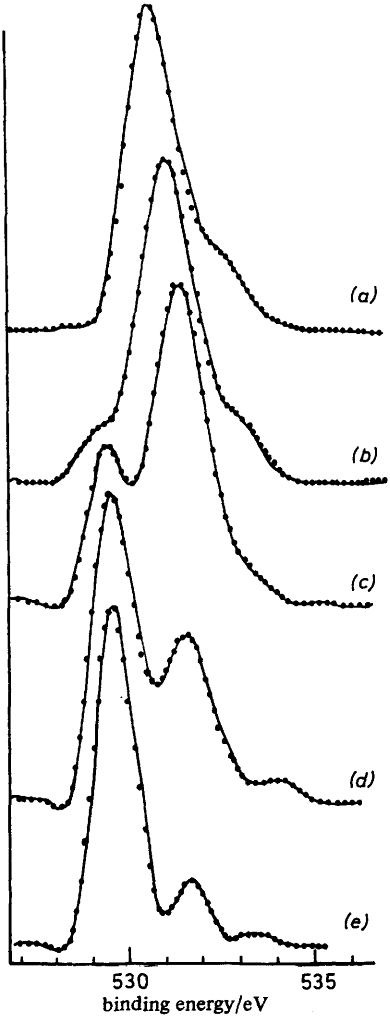

**Fig. 3.** Deconvoluted O(1*s*) spectra for thermal decomposition of $\beta$NiO(OH); see fig. 1 above. (Scaled to same maximum.)

for example, in the O(1*s*) spectrum of $\alpha$FeO(OH)[15, 16]. It is not until the sample is heated to 423 K and above that two distinct O(1*s*) peaks can be observed; the major component at 531.4 eV and a shoulder around 529.7 eV [fig. 1(*b*)–(*d*)]. There is a concomitant transfer of intensity from high to low binding energy in the Ni($2p_{3/2}$) spectra consistent with the reduction of $Ni^{3+}$ to $Ni^{2+}$. The final spectra obtained in the thermal decomposition (773 K) are typical of NiO[fig. 1(*e*) and 2(*e*)].

Fig. 3 shows the results of refining the O(1*s*) spectra using a deconvolution method[17] which smooths and subtracts background and removes broadening in the spectra arising from the finite X-ray width and analyser broadening. The spectrum in fig. 3(*a*) was obtained before thermal decomposition and shows clearly the presence of a shoulder to the high-binding-energy side of the main O(1*s*) peak at 533 eV in the region expected for intercalated water. In fig. 3(*b*) after heating to 423 K three peaks can be seen: the low-binding-energy peak which later predominates becomes apparent, the main peak now shifted 0.8 eV to higher binding energy and the smaller peak at *ca.* 533 eV. The results of curve-fitting the O(1*s*) data in fig. 3 using a method based on that of Fraser and Suzuki[17] are shown in fig. 4.

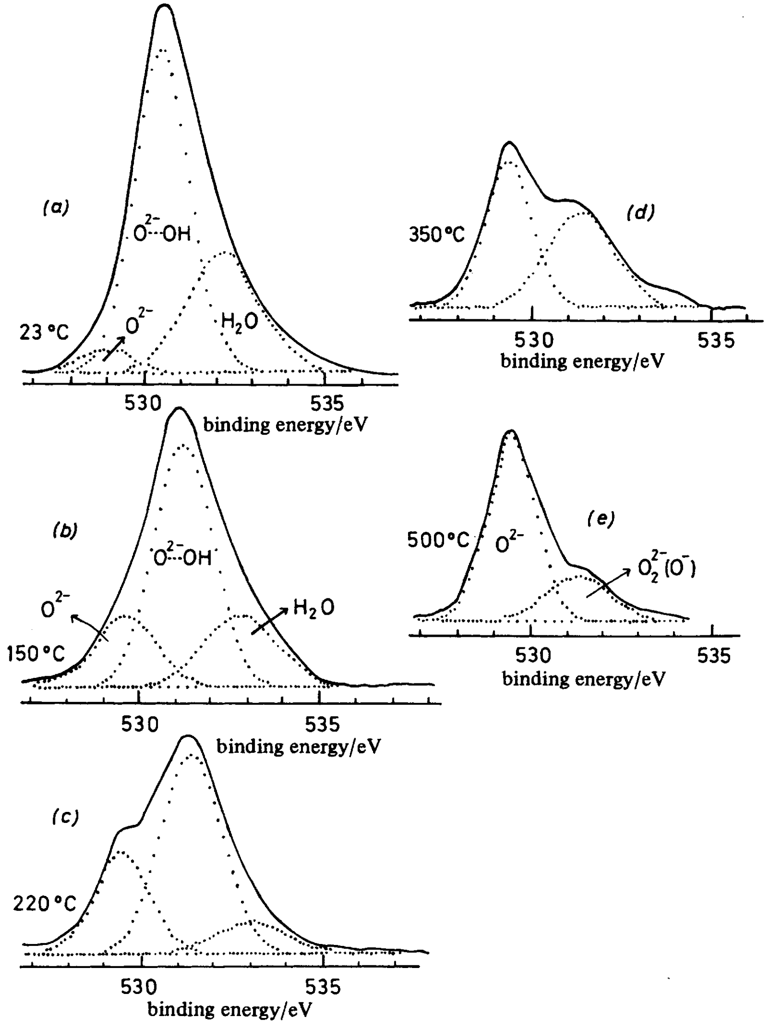

**Fig. 4.** O(1*s*) curve-fitted spectra for βNiO(OH) and during thermal decomposition with peak assignments. (*a*) 296, (*b*) 423, (*c*) 493, (*d*) 623 and (*e*) 773 K.

## HYDROGEN INTERACTION IN βNiO(OH)

It has been suggested, in connection with αFeO(OH), that the hydroxyl proton has some interaction with the $O^{2-}$ oxygen because the oxide O(1*s*) peak was slightly shifted towards that of the hydroxide O(1*s*) peak compared with the O(1*s*) peak characteristic of $O^{2-}$ present in $\alpha Fe_2O_3$.[15] It seems that a greater interaction of the proton between the two oxygens in βNiO(OH) could explain the observed single O(1*s*) peak (fig. 1) and a consideration of the crystal structure of βNiO(OH) shows that this is indeed a possibility. $\beta$NiO(OH) adopts a brucite or C6 structure with a hexagonal unit cell of dimensions $a = 2.82$ Å and $c = 4.85$ Å.

Each nickel atom is surrounded by six oxygen atoms, three lying above the nickel plane and three below. Water molecules are incorporated in a random way between some of the layers. No information about the location of the H atom is available, but the oxygen–oxygen distance of 2.95 Å is within the range observed for medium strength O—H $\cdots$ O hydrogen bonds.[18] Furthermore, some preliminary i.r. experiments of $\beta$NiO(OH) evacuated to $7 \times 10^{-4}$ Torr for 1.5 h at room temperature show a large, very broad absorption from 3700 to 3000 cm$^{-1}$ indicating the presence of hydrogen-bonded OH groups. Thus $\beta$NiO(OH) might be represented as sheets of $Ni^{3+}$ ions and OHO layers as in fig. 5 with the intercalated water participating in the stabilisation of the $OHO^{3-}$ groups.

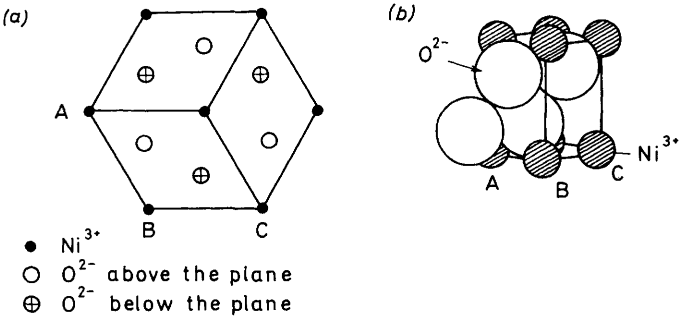

**Fig. 5.** Two views of $\beta$NiO(OH) showing (*a*) the plane of Ni atoms and (*b*) the Ni and OH $\cdots$ O layers

The thermal decomposition of $\beta$NiO(OH) may therefore be represented as

$$2\beta\text{NiO(OH)(s)} \rightarrow 2\text{NiO(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} + \text{H}_2\text{O(g)}.$$

Loss of an OH group from the OHO aggregate, and the ensuing reduction of $Ni^{3+}$ to $Ni^{2+}$ in nickel oxide, disrupts the OHO bonds in surrounding groups. This would account for the splitting of the single O(1*s*) peak at 530.5 eV into low- and high-binding-energy peaks; the 529.7 peak is due to the $O^{2-}$ ions of the newly formed NiO and the $Ni^{3+}$–$O^{2-}$ interaction, and the 531.5 eV peak is due to the hydroxyl oxygens in the isolated NiO(OH) groups. However, the intensity of the high-binding-energy peak is initially larger than that of the 529.7 eV peak, unlike the behaviour seen for FeO(OH) in which the initial O(1*s*) spectra show two peaks that are approximately representative of the 1:1 stoichiometry of the oxyhydroxide.

This led us to consider the mechanism of decomposition. As in all heterogeneous decompositions, release of product molecules ($H_2O$ and $O_2$ in this case) with the associated change in crystal structure results in considerable disruption of the reaction interface. Formation of molecular oxygen at this stage demands a rapid mobility of the oxygen ions. This mobility, while likely to occur at elevated temperatures, would be quenched on cooling to room temperature prior to obtaining spectra. At this point the 'atomic' oxygen may be entrained within the incipient 'surface' NiO structure; we should recall that X.p.s. is sensitive to only the outermost *ca.* 20 Å of a solid. It is this excess oxygen in the surface region that we anticipate gives rise to the intensity at the 531.4 eV position in addition to that expected for $OH^-$ (if present). Since no significant concentration of surface hydroxyls will exist after heating the oxyhydroxide to 773 K in a vacuum, when both evolution of $O_2$(g) and $H_2O$(g) have ceased, we assign

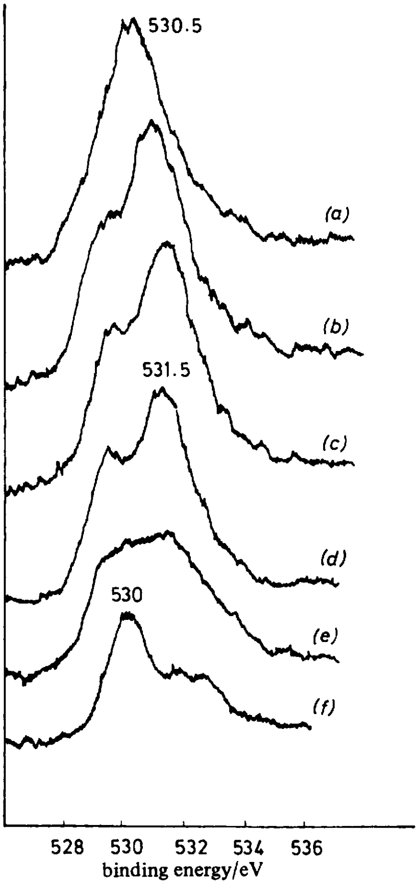

**Fig. 6.** O(1*s*) spectra for 'nickel peroxide' at 296 K and an ambient pressure of $5 \times 10^{-7}$ Torr (*a*) and after heating (*b*) 423, (*c*) 453, (*d*) 493, (*e*) 623 and (*f*) 773 K.

the 531.4 eV peak to $O_2^{2-}$ species formed by interaction of oxygen atoms trapped in the NiO structure with lattice oxygen. Note that there is a correlation between the observed O(1*s*) binding energy and the amount of negative charge available for delocalisation on the oxygen atoms in each of the species, *i.e.* the lowest-binding-energy O(1*s*) peak has been assigned to $O^{2-}$ with a maximum charge per oxygen atom of 2; $OHO^{3-}$, with a maximum charge per O atom of 1.5, has an intermediate binding energy, while both $O^-$ and $O_2^{2-}$, with a maximum charge per oxygen atom of − 1, have the same binding energy as $OH^-$, which also has a maximum charge per O atom of − 1. $O^-$ species present at a zinc oxide surface have also been shown to have an O(1*s*) peak at 531.5 eV.[19] The curve-fitted components (fig. 4) are therefore assigned as shown.

## DECOMPOSITION OF 'NICKEL PEROXIDE'

The thermal decomposition of 'nickel peroxide' was also followed by X.p.s. Fig. 6 and 7 show the O(1*s*) and Ni($2p_{3/2}$) spectra observed. It can be seen that the as-prepared nickel peroxide and $\beta$NiO(OH) exhibit identical O(1*s*) and Ni(2*p*) spectra. Furthermore,

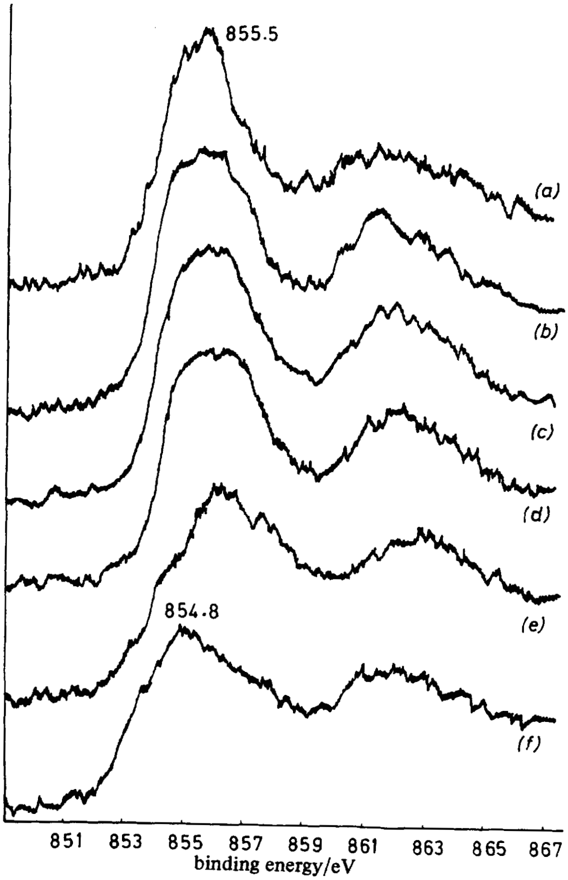

**Fig. 7.** Ni($2p_{3/2}$) spectra corresponding to the O($1s$) spectra of fig. 6.

the spectra obtained during thermal decomposition show the same behaviour. Molecular oxygen and water vapour were the only gaseous products observed during decomposition. These observations are, in general, compatible with those of Bond and Tripathi,[5] who have suggested that the mechanism of the decomposition of 'nickel peroxide' involves the following steps:

$$Ni_2O_3 \cdot 2H_2O(s) \rightarrow Ni_2O_3 \cdot H_2O(s) \rightarrow 2NiO(s) + \tfrac{1}{2}O_2(g) + H_2O(g).$$

However, because $\beta$NiO(OH) is an alternative representation with the same stoichiometry as $Ni_2O_3 \cdot H_2O$ but having a well defined crystal structure which we have found essential for our model to explain the observed X.p.s. data, we prefer the formulation $\beta$NiO(OH) for nickel peroxide. We therefore suggest that the mechanism of 'peroxide' decomposition involves the removal of intercalated water followed by the reaction

$$2\,NiO \cdot OH \rightarrow 2\,NiO + H_2O + \tfrac{1}{2}O_2.$$

The essential difference between us and Bond and Tripathi[5] is in our suggestion that the 'peroxide' be represented as $\beta$NiO(OH)$\cdot H_2O$ rather than $Ni_2O_3 \cdot 2H_2O$.

During evacuation at room temperature the mass spectra showed that $H_2O$ was being continuously evolved, accompanied by an increase in asymmetry to the low-binding-energy side of the main O(1*s*) peak. The water present in the structure is clearly necessary to preserve the oxygen equivalence [as indicated by the O(1*s*) spectra], and this equivalence is destroyed as water is removed even to some extent at room temperature.

## CONCLUSIONS

The investigation has shown that under the conditions used 'nickel peroxide' and synthesized $\beta$NiO(OH) are, when studied by X.p.s., seen to be spectroscopically identical. They both decompose on heating to give defective NiO, water vapour and molecular oxygen. Before decomposition both samples exhibit a single peak in the O(1*s*) spectra at 530.5 eV, a value intermediate between the 529.7 eV peak attributed to the $O^{2-}$–$Ni^{2+}$ interaction and the 531.4 eV peak of the hydroxyl species. An explanation proposed to account for this is given in terms of the structure of $\beta$-NiO·(OH) with intercalated water molecules providing an environment for spectroscopically (X.p.s.) identical oxygen species. When, on heating, hydroxyl groups are lost as water, the equivalence of the oxygen species disappears and the central O(1*s*) peak is replaced by the peaks at 529.7 and 531.4 eV observed with NiO and $Ni(OH)_2$. The equivalence of the oxygens seems to be facilitated by the relatively large amounts of intestitial water present, because as water is removed by evacuation (even at room temperature) a growth of intensity at *ca.* 529.7 eV is observed.

In the early stages of decomposition (*e.g.* at 493 K) the intensity of the O(1*s*) peak at 531.4 eV exceeds that at 529.7 eV, instead of the expected equal contribution to both oxide and hydroxide peaks. This is attributed to the 531.4 eV peak being a composite, reflecting both $OH^-$ and $O^-$ (or $O_2^{2-}$) species, the latter being associated with defective nickel oxide. The Ni(2*p*) spectra support these assignments.

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