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Oxidation of β -Ni(OH)₂: positron lifetime study of a heterogeneous solid

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Abstract. Positron lifetime spectroscopy was used to characterise the β -Ni(OH)₂/ β -NiOOH electrode system. The lifetime parameters for both chemically and electrochemically treated samples are presented. Three different stages in the oxidation-reduction process were observed and identified. For intermediate-oxidation states the samples were assumed to be heterogeneous and the interface between the differently oxidised phases proved to be an effective positron trap. The positron lifetime parameters provided valuable information about the oxidation processes occurring in different ways in the chemically and the electrochemically treated samples.

1. Introduction

Nickel hydroxide (Ni(OH)₂) is one of the most important electrode materials. Yet its transitions during the oxidation process are not clearly understood. Conventional methods of structural characterisation (e.g. x-ray diffraction) provide only limited information about the transformations of this material because of the similar crystallographic structure of Ni(OH)₂ and nickel oxyhydroxide (NiOOH). Therefore much work has been done on this topic, in particular recently [1, 2].

One of the best descriptions of the electrochemical oxidation-reduction of Ni(OH)₂ was given in [3] on the basis of electrode potential measurements. It was found that the oxidation process could be divided into three stages. The first is between the oxidation states of 2.00 and 2.25. In this range of oxidation the electrode material is roughly, say, a solid solution of an increasing amount of β -NiOOH in the β -Ni(OH)₂ matrix. Between the oxidation states of 2.25 and 2.75, two phases coexist with different oxidation states. The first has an oxidation state of about 2.25 and the second of about 2.75. In this range of oxidation, only the relative fraction of the high-oxidation phase increases while that of the low-oxidation phase decreases. Above the oxidation state of 2.75 the electrode material becomes homogeneous again, i.e. it forms a solid solution. The reduction process takes place in a similar way.

In our earlier work, we confirmed the outlined mechanism of the oxidation-reduction process on electrochemically treated samples with the help of positron lifetime spectro-

scopy and observed the formation of a positron trap in the heterogeneous range [4]. In this work, we give the results of measurements performed on chemically oxidised samples and compare these results with those of electrochemical oxidation.

2. Experimental details

The starting material was the same β -phase $\text{Ni}(\text{OH})_2$ for both electrochemical and chemical oxidation. It was precipitated from nickel sulphate solution by potassium hydroxide (KOH) at room temperature. To obtain good electrical contact during the electrochemical treatment, the samples were mixed with 20% graphite. The detailed description of the sample preparation and the electrochemical oxidation–reduction process can be found in [4].

The chemical oxidation of the $\text{Ni}(\text{OH})_2$ was carried out at 80 °C in 0.1 mol dm⁻³ KOH solution by sodium hypochlorite [1], which was prepared by the saturation of 2.5 mol dm⁻³ KOH with Cl₂ gas. This oxidation procedure was much quicker than the electrochemical process. The oxidised samples were washed free of oxidising agent and dried in a desiccator over phosphorus pentoxide (P₂O₅) in vacuum. These samples were mixed with graphite, too, in order to facilitate comparison of results between the differently manufactured samples.

Lifetime spectra were recorded with a conventional fast–slow coincidence system, the time resolution of which was 330 ps. Spectra were evaluated as three components by the POSITRONFIT EXTENDED computer program [5]. However, these components were scarcely identifiable because of the two lifetimes of the graphite and the three lifetimes of the pure material [4].

3. Results and discussion

The main results are shown in figure 1(a) for electrochemically prepared samples and in figure 1(b) for chemically prepared samples. The changes in τ_3 and I_3 measured on the oxidised samples can be seen in figure 2. These latter parameters did not change significantly in the electrochemically reduced samples (τ_3 was about 2.5 ns and I_3 about 0.3% in every case); therefore, they are not given in the figures.

Of the lifetimes, τ_3 is the only identifiable one. On the basis of our earlier measurements on fine-grained and rough-grained pure $\text{Ni}(\text{OH})_2$ [4], we related it to the annihilation of oxidised positronium atoms trapped at the surface of $\text{Ni}(\text{OH})_2$. Therefore, the decrease in I_3 indicates the decreasing $\text{Ni}(\text{OH})_2$ content of the surfaces of grains. Accordingly, we can conclude that during chemical oxidation the surface of a $\text{Ni}(\text{OH})_2$ grain is oxidised at the very beginning of the oxidation process (figure 2). On the contrary, during electrochemical oxidation, many $\text{Ni}(\text{OH})_2$ ‘islands’ remain unchanged even at high-oxidation states.

Apart from the values of I_3 and τ_3 , there are hardly any differences between the annihilation characteristics of the unoxidised and the fully oxidised samples (figure 1). This is in very good agreement with the almost identical crystallographic structure of $\text{Ni}(\text{OH})_2$ and NiOOH [6].

During the electrochemical oxidation process the lifetime parameters scarcely changed in the first region (an oxidation state range of 2.00–2.30) where the material was homogeneous. This indicates no discernible structural change in the sample. At an

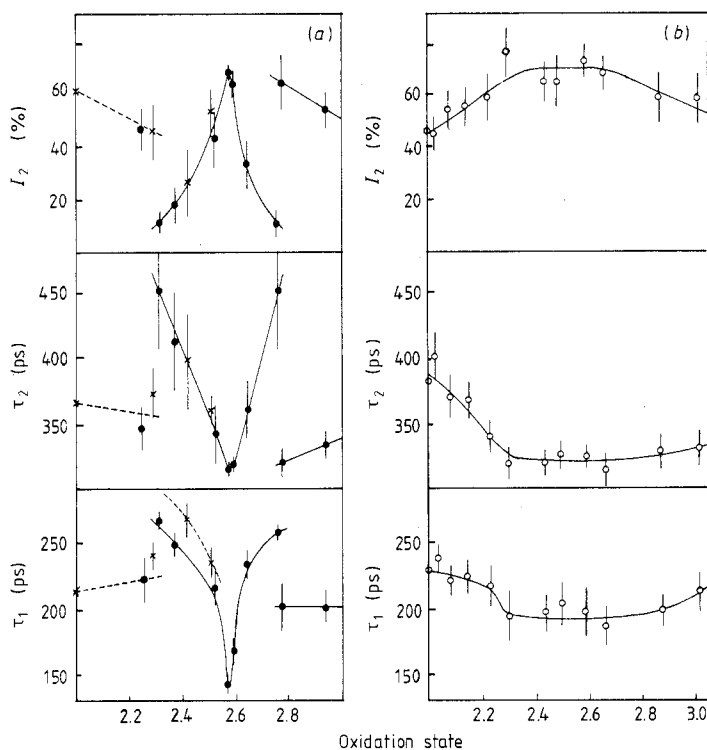


Figure 1. Lifetime components τ_1 , τ_2 and intensity I_2 for electrochemically oxidised (---x---), reduced (—●—) and chemically oxidised (—○—) samples. Note that $I_1 \approx 100 - I_2$ in all cases.

oxidation state of 2.30 an unexpected 'jump' appeared in the annihilation curves. This jump was associated with the appearance of a new positron trap in the samples and thus with a new lifetime component in the spectra [4]. I_2 increased to the oxidation state of about 2.50 and then decreased again. This observation suggests that the concentration of the assumed trapping centres changes in a similar way. Only the interface between the high-oxidation and low-oxidation phases should show such a behaviour [3, 4]; therefore, it must be due to the observed positron trap.

At an oxidation state of 2.75 a second jump was observed, i.e. the positron trap disappeared from the sample. Further oxidation caused small changes in the annihilation parameters, as was expected during the oxidation of the solid solution. The reduction and oxidation processes provide very similar changes in the lifetime parameters. The only exception is τ_3 which does not change during reduction of the samples. The formation of the pure Ni(OH)_2 only at the end of the reduction [3] is confirmed by this.

The chemical oxidation shows very different curves for the annihilation parameters (figure 1). In the first homogeneous stage of the oxidation, τ_2 decreases and I_2 increases remarkably, while the decrease in τ_1 is slight but significant as well. These changes suggest a definite modification of the structure of samples. Between the oxidation states of 2.30 and about 2.70, no change was observed in the annihilation characteristics of samples. Note that in this range the lifetime and

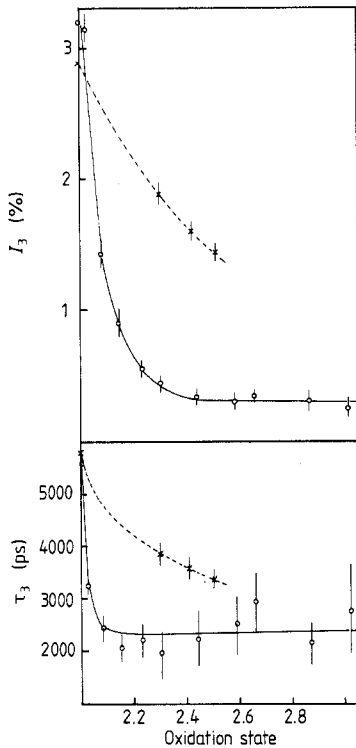


Figure 2. τ_3 and I_3 values for electrochemically (---×---) and chemically (—○—) oxidised samples.

intensity parameters are almost identical with those measured on electrochemically treated samples at the maximum concentration of the above-mentioned positron trap. Above an oxidation state of 2.70, only small changes were observed in the lifetime parameters and no difference was detected between chemically and electrochemically treated samples.

From the figures, it is obvious that the chemical and electrochemical oxidation processes take place in different ways. The rapid decreases in I_3 and τ_3 at the beginning of the chemical oxidation suggest that the oxidation begins at the surfaces of grains. This also indicates that a significant over-oxidation can take place at the surfaces. (This means that the local oxidation state at the surfaces is higher than the average value of the entire sample.) The oxidation rate is high at the surfaces of grains and the bulk has no time to reach an equilibrium state. The presumption of over-oxidation can be confirmed by the remarkable changes in I_2 and τ_2 between the oxidation states of 2.00 and 2.30, indicating a significant structural modification, while no similar change was observed in electrochemically treated samples.

The continuous changes in I_2 and τ_2 can be explained by the continuous formation of interfaces between the high-oxidation and low-oxidation phases due to over-oxidation. This can also explain the fact that in this case no jump was obtained in the curves of annihilation parameters. It is clear that the appearance of new phases and, therefore, of interfaces cannot be connected with a particular oxidation state of the sample.

The constant values of lifetime parameters between the oxidation states of 2.30 and 2.70 suggest that a large number of interfaces, i.e. positron traps, exist in this

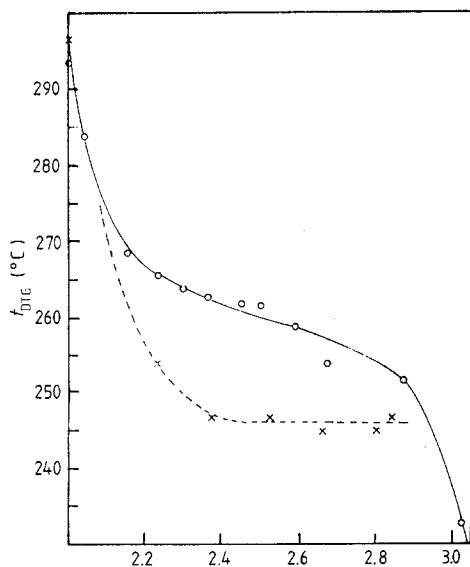


Figure 3. Temperature t_{DTG} of water loss against the oxidation state for electrochemically (---x---) and chemically (—o—) treated samples.

range of oxidation. The lack of jumps in the annihilation parameters at high-oxidation states indicates that the over-oxidation could also be significant in this range.

Over-oxidation was not expected during electrochemical oxidation, where the low oxidation–reduction rate made it possible for the material to achieve equilibrium. According to the small structural modification of the solid solution, almost no changes were observed in lifetime parameters in the two homogeneous stages of oxidation. The jumps observed in annihilation curves can be related to the immediate formation of the differently oxidised phases, i.e. to the formation of an interface, at a particular oxidation state.

The rapid chemical oxidation has further consequences. As the experimental circumstances are hardly controllable, the differently oxidised phases have uncertain chemical combinations. In this process, many metastable phases are expected to form, i.e. oxidation above an oxidation state of 2.25 should not lead to the formation of another phase [7]. This assumption is confirmed by the differential thermogravimetric (DTG) curves of the oxidation processes (figure 3). During electrochemical oxidation the temperature t_{DTG} at which there is water loss is constant above an oxidation state of 2.25, indicating the existence of a well defined phase in this range. On the contrary, during chemical oxidation, t_{DTG} decreases continuously, which indicates continuous modification of the chemical combination of phases. The decreasing DTG curve of the chemical oxidation process also confirms the reliability of the original assumption of over-oxidation.

Summarising the results, we can conclude the positron lifetime spectroscopy is a valuable tool in the investigation of the $\beta\text{-Ni(OH)}_2/\beta\text{-NiOOH}$ electrode system. The heterogeneity of the material could be confirmed by lifetime measurements for both electrochemically and chemically treated samples. The interface between the high-oxidation and low-oxidation phases proved to be an effective positron

trap. Moreover, over-oxidation of the chemically oxidised samples could be assumed on the basis of our measurements.

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