

SURFACE CHARACTERISATION OF Ni(OH)₂ MODIFIED ELECTRODES OBTAINED BY THE DERIVATISATION OF NICKEL HEXACYANOFERRATE(NiHCF) FILMS

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The nickel oxide/ oxyhydroxide redox system prepared as a thin film on electrode surface by a novel route starting from nickel hexacyanoferrate, has been found to possess interesting electrochemical, electrochromic and electrocatalytic properties as revealed by our studies. To understand the unique differences of this film electrode (Type 1) from that of the conventional nickel oxide electrode (Type 2) surface characterisation studies were carried out. Impedance measurements, XRD and SEM studies carried out on these two type of electrodes reveal marked differences in the Type 1 Ni(OH)₂ film to be more electroactive, uniform surface structure and facilitating electron transfer at a faster rate compared to Type 2 electrode. The reason for the observed differences are attributed to the method of preparation.

INTRODUCTION

Recently it has been reported from our laboratory [1] that Ni(OH)₂ modified electrodes (Type 1) prepared from Nickel hexacyanoferrate (NiHCF) films are found to have very good electrocatalytic properties. The analytical utility of the Type 1 electrodes has also been explored for biologically important compounds [2]. Cataldi et al. have evaluated the XPS changes when NiHCF films are converted to Ni(OH)₂ species by cycling in alkali [3]. Ni(OH)₂ films are usually formed by [4-6] cycling nickel electrodeposits in strong alkali (Type 2 electrodes). Our experimental observations show that electrocatalysis of organic compounds like sugars and alcohols occurs at the Nihydroxide/oxyhydroxide redox potential. Electrocatalysis is shown by the enhancement of anodic peak of Ni(OH)₂ [1]. In the case of Type 2 electrodes [7] a new oxidation peak corresponding to catalysis of organic compounds like sugars and alcohols is obtained at a potential much more positive than Ni(OH)₂ potential. This difference in mechanism of catalytic oxidation has also been reported by earlier workers in this field [8-10]. The difference in the properties may be attributed to the existence of two different forms of NiOOH γ and β and Ni(OH)₂ α and β as suggested by several workers. It is well known that α form is more electro-active and it is converted to γ form of NiOOH on oxidation. The difference in properties reported prompted us to study the structural differences associated with the nickel oxide prepared by two different methods. Impedance measurements, XRD and SEM are used in the

present investigation to characterize Type 1 and Type 2 electrodes and the results are reported.

EXPERIMENTAL

Preparation of Type 1 electrodes

Type 1 electrodes are prepared by subjecting the glassy carbon electrode to electrochemical cycling at 1.0 V/s between 0 and 1.0V for 30 mins in a clear solution of 0.5 mM NiSO₄ in 0.5mM K₃[Fe(CN)₆] + 0.1M HCl + 0.5M KCl [10]. By this method NiHCF films are formed on the electrode surface. On cycling the NiHCF electrodes in alkaline solution Ni(OH)₂ \rightarrow NiOOH + H⁺ + e film is formed on the electrode surface.

Preparation of Type 2 electrode

Type 2 electrodes are prepared by subjecting the glassy carbon electrode to electrochemical cycling at 20 mV/s between 0 and +0.8V in a solution of 5 mM NiSO₄ in 8N KOH.

Preparation of electrode substrates for XRD measurements:

Glassy carbon electrodes (Tokai GC; 4 mm dia) are used for the preparation of Type 1 and Type 2 Nickelhydroxide modified electrodes. XRD measurements were made using the instrument JEOL, JDX 8030. The instrument has provision to find out the matching peaks for standard species.

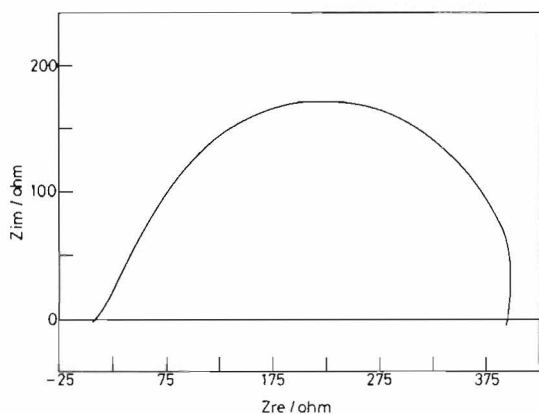


Fig.1: Impedance spectrum for Type 1 electrode

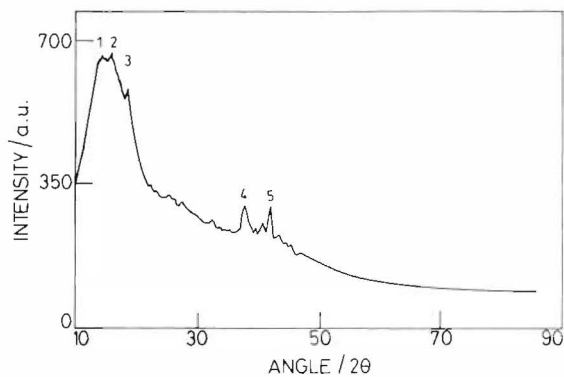


Fig.4: XRD pattern for Type 2 electrode

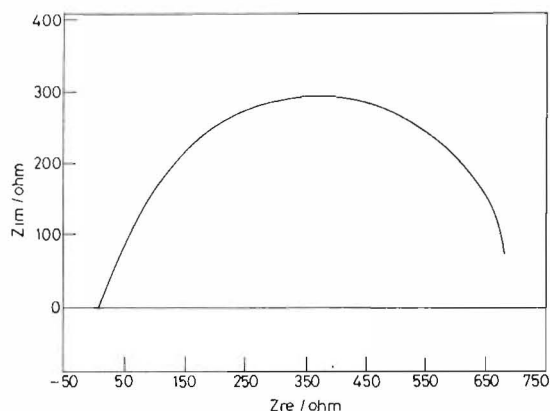


Fig.2: Impedance spectrum for Type 2 electrode

Preparation of electrode substrate for SEM measurements:

Glassy Carbon electrodes (Tokai GC, 2 mm dia) are used for the preparation of Type 1 and Type 2 modified electrodes.

Scanning electron micrographs were recorded using JEOL 30CF instruments. The figures given represent a magnification of nearly 1600. Each cm corresponds to 5.5 μm in the micrographs.

Impedance Analysis:

Impedance measurements were made using PAR (EG&G) Model 398 instrument. The frequency range covered is 100 mHz to 100 KHz. Three electrode cell is used for the investigations. Glassy carbon is the working electrode. Platinum is used as the counter electrode and Hg/HgSO₄ is used as the reference electrode.

Table.I: Comparison of XRD observed values of γ NiOOH with standard values for Type I electrode

Standard values for NiOOH			Observed values		
2θ	d value	Intensity	2θ	d value	Intensity
12.826	6.897	100	12.737	6.994	83
25.906	3.436	80	25.997	3.425	61
37.099	2.421	10	37.006	2.427	48
37.938	2.370	80	41.316	2.183	47
41.127	2.193	5	43.304	2.088	44
43.209	2.092	80			
48.383	1.880	10			
51.597	1.770	80			
58.769	1.570	10			
63.174	1.471	10			
66.204	1.410	60			
68.431	1.370	60			
71.338	1.3210	10			

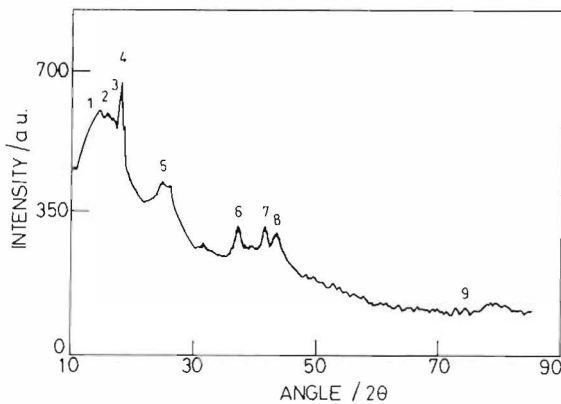


Fig.3: XRD pattern for Type 1 electrode

TABLE II: Comparison of XRD values of γ NiOOH with standard values for Type II electrode

Standard values for NiOOH			Observed values		
2 θ	d value	Intensity	2 θ	d value	Intensity
18.350	4.831	100	18.439	4.808	88
37.285	2.410	80	37.472	2.398	45
66.731	1.401	80			

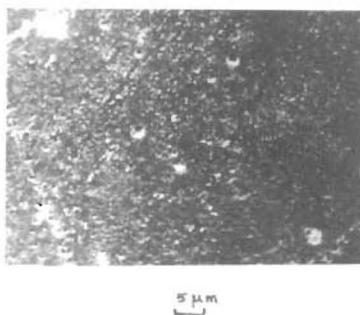


Fig.5: SEM picture of Type 1 electrode

RESULTS AND DISCUSSION

Fig.1 represents the impedance spectrum obtained for Type 1 electrode. The spectrum shows a semicircular region. R_{ct} was determined to be around 375 ohms. Fig.2 represents the impedance spectrum obtained for Type 2 electrode. The spectrum shows a similar behaviour and R_{ct} was found to be 700 ohms. By substituting R_{ct} value in the equation

$$R_{ct} = RT/nFI_0 \dots\dots (1)$$

I_0 value was computed for both the electrodes. The I_0 values correspond to 6.96×10^{-5} A/cm² and 3.72×10^{-5} A/cm² and K_s values calculated from the equation,

$$K_s = I_0/nFAC \dots\dots (2)$$

are 2.4s and 1.28s for Type 1 and Type 2 electrodes respectively. This result clearly shows that electron transfer rate constant is more facile in the case of Type1 electrode.

Fig. 3 represents the XRD pattern for the Type 1 electrode. The observed peak values match with that of γ -NiOOH as given in Table I. Fig.4 represents the XRD pattern for Type 2 electrode. The observed peak values match with that of γ -NiOOH. which is reflected from the data in Table II.

The peaks due to Ni(OH)₂ are not observed in both the cases. This suggest NiOOH is the stable species that is present in the surface and ex-situ measurements show the presence of NiOOH only. Many surface characterisation techniques, including Atomic Force Microscopy reveal that α form is the electroactive form which converts to γ form on oxidation.



Fig.6:SEM picture of Type 2 electrode

On ageing α form slowly changes to β form. Therefore, Type 1 electrode prepared through NiHCF films contains the electrochemically active form α Ni(OH)₂/ γ NiOOH and Type 2 electrode contains the β Ni(OH)₂/ β NiOOH form [12].

Fig. 5 represents the scanning electron micrograph (SEM) of Type 1 electrode. The surface appears to be uniform film without much defects. Fig. 6 represents the SEM of Type 2 electrode. The surface contains particles of redox species dispersed at different points. Hence it is concluded that Type 1 electrode prepared through NiHCF forms a uniform film whereas Type 2 electrode prepared from 8N KOH contain particles distributed at different points and it is not uniform.

CONCLUSION

Surface characterization by three different techniques reveals that Type 1 Ni(OH)₂ films are more electroactive, possess uniform surface structure and electron transfer proceeds at a faster rate at these surfaces.

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