

Analysis of active material and additive distributions in a nickel hydroxide electrode by SEM/EDX techniques

Arnaldo Visintin*, Anaba Anani**, Supramaniam Srinivasan and A. John Appleby
Center for Electrochemical Systems and Hydrogen Research, Texas Engineering Experiment Station, Texas A&M University System, College Station, TX 77843-3402 (USA)

Lisa Donaghe

Electron Microscopy Center, Texas A&M University, College Station, TX 77843 (USA)

Hong S. Lim

Electron Dynamics Division, Hughes Aircraft Company, Torrance, CA 90505 (USA)

(Received January 25, 1994; accepted in revised form March 8, 1994)

Abstract

Cobalt and cadmium additive distributions in the active material across the thickness of a nickel electrode were determined by using scanning electron microscopy and energy dispersive X-ray analysis techniques. The nickel oxide/hydroxide active material is impregnated in small pores (10 to 15 μm) of the nickel substrate of the electrode. To avoid possible interference by the nickel metal substrate, the additives and ionic nickel were analyzed on micro-spots in the active material on a cross section of the electrode. The atomic ratio of nickel to oxygen at each analytical point was used to confirm that the analyses were carried out at spots constituting pure active materials only, without any contamination from the nickel substrate/metal. Results showed that cobalt and cadmium additives were more concentrated at the surface than the bulk for electrodes prepared by the electrochemical impregnation technique. Trends in the distributions of the individual elements (additives) did not change after cycling of the electrodes (up to about 50 cycles) in flooded cell configurations.

Introduction

Additives are commonly used in nickel electrodes [1] for alkaline batteries such as Ni/Cd, Ni/MH_x and Ni/H₂. The active material of the nickel electrode is nickel oxide/hydroxide. Many different additives have been used to improve the electrode performance [2]. Among the additives, cobalt showed many beneficial effects such as increase in the utilization of the active material of the nickel oxide electrode [3-5], dimensional stability, reduced electric resistance [6] and improved electrochemical reversibility [7]. Cadmium addition is also believed to improve the electrode performance through improvement of the conductivity of the active material and raising the oxygen

*Present address: INIFTA-UNLP, C.C. 16, Sucursal 4, 1900 La Plata, Argentina.

**Present address: Energy Products Operations, Motorola, Inc., 8000 W. Sunrise Boulevard, Plantation, FL 33322, USA.

overtoltage [8]. A recent micro-calorimetric study showed that cadmium additive in the presence of cobalt might reduce self-discharge reaction of a Ni/H₂ cell [9, 10].

Undesirable inequalities in the distribution of additives in the active material of a nickel electrode may arise during electrochemical impregnation from nonuniform current distribution in the porous structure and also from the differences in solubility product of the different hydroxides. Uneven distribution of additives within the active material may also play a diminished role during activation of the active material; the eventual utilization of the electrode will depend strongly on the distribution of additive, and as a consequence, full utilization is seldom attained in practical electrodes. It is thus desired to have even distributions of additives in the electrode in order to achieve optimum effects of the additives. However, a comprehensive study of the distribution of additives had not been previously undertaken. This was due, in large part, to experimental difficulties in analyzing the additives which are imbedded in small pores (10 to 15 μm) within the nickel substrate of the electrode. The difficulty has been attributed to possible interference by the nickel substrate during the analysis, contributing to the overall material count of nickel oxide/hydroxide active material. In this report, we have discussed an effective technique for the analysis of the distribution of additives across the thickness of the electrode and between adjacent nickel particles.

Experimental

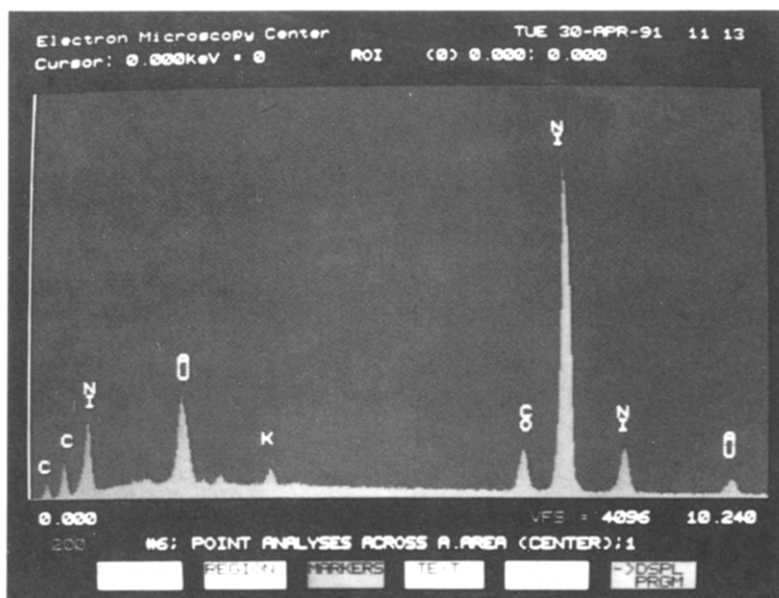
The electrode samples used in this work were sintered types and of similar nature to those used in aerospace Ni/H₂ cells 'fly-type electrodes'. The electrodes were prepared by an electrochemical impregnation technique in an aqueous alcoholic bath containing nitrates of nickel and additive metals (Co and Cd). Electrode substrate was a dry powder sintered nickel plaque which was $\sim 80\%$ porous [1]. Test sample electrodes contained additives of either Co alone or a combination of Co and Cd. Thickness of the electrodes were within 0.7 to 0.8 mm.

The scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) equipment used in this study was a JSM model 6400 scanning electron microscope, equipped with a Noran I-2 EDX unit. Experimental samples were prepared by potting the electrodes in an Araldite epoxy mixture. The potting was carried out under vacuum to avoid formation of air bubbles in voids of the electrode samples. The epoxy was cured at 45 °C. The cross section of the electrode in the potted epoxy was polished with 0.3 to 1 μm alumina powder solutions.

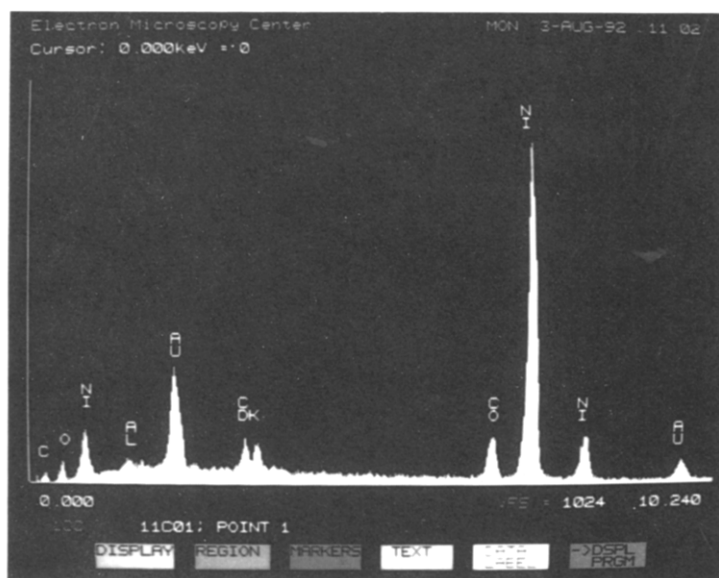
Results and discussion

Surface morphology and active material distribution

The active material constituents in the various electrode samples were analyzed using both the EDX and atomic absorption techniques. Figure 1 shows representative EDX spectra of the active material for electrode samples of the two types described in the previous section, i.e., with Co additives only, and with Co and Cd additives together. The spectra were taken in areas which appeared to be active material, and thus the oxygen peak observed in the spectra is an indication of the presence of the active components – Ni, Co, O and Ni, Co, Cd, O – respectively. Atomic absorption measurements yielded elemental contents which are consistent with the impregnation electrolyte constitution, the ppm of Cd increasing as the concentration in the impregnation solution increases (Table 1).



(a)



(b)

Fig. 1. Representative EDX spectra of the active material in the electrode with (a) Co, and (b) Co and Cd additives.

Representative SEM images ($\times 75$ to $\times 80$) of a polished electrode cross section of a typical sample before and after about 50 cycles are shown in Fig. 2. Large light circular areas represent cross sections of Ni wire screen. Light microscopic areas

TABLE 1
Elemental composition of nickel hydroxide electrodes with cobalt and cadmium additives by EDX^a

Sample no.	Element composition						
	Cadmium		Cobalt		Nickel		Iron ^c
	(ppm)	(concentration ^b × 10 ³)	(ppm)	(concentration × 10 ²)	(ppm)	(concentration × 10 ¹)	(ppm)
1	12.08	0.755	20.72	1.295	386.6	2.420	0.054
3	21.26	1.328	21.02	1.313	413.1	2.58	0.046
5	28.83	1.801	18.10	1.131	389.2	2.430	0.045
7	14.97	0.936	52.08	3.255	386.1	2.410	0.036
9	24.30	1.518	52.2	3.262	405.3	2.533	0.032
11	32.33	2.020	47.15	2.946	396.1	2.475	0.031

^aBath composition

Sample 1: 1.92 M in Ni²⁺, 0.08 M Co²⁺ and 0.05 M Cd²⁺.

Sample 3: 1.92 M in Ni²⁺, 0.08 M Co²⁺ and 0.10 M Cd²⁺.

Sample 5: 1.92 M in Ni²⁺, 0.08 M Co²⁺ and 0.10 M Cd²⁺.

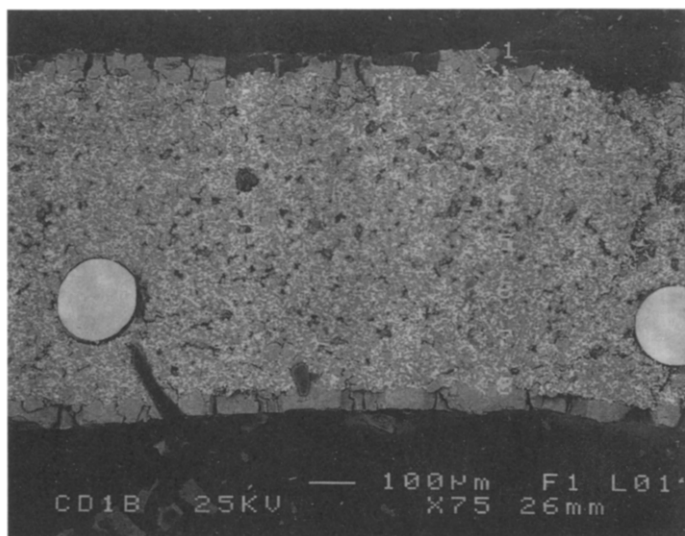
Sample 7: 1.82 M in Ni²⁺, 0.18 M Co²⁺ and 0.05 M Cd²⁺.

Sample 9: 1.82 M in Ni²⁺, 0.18 M Co²⁺ and 0.10 M Cd²⁺.

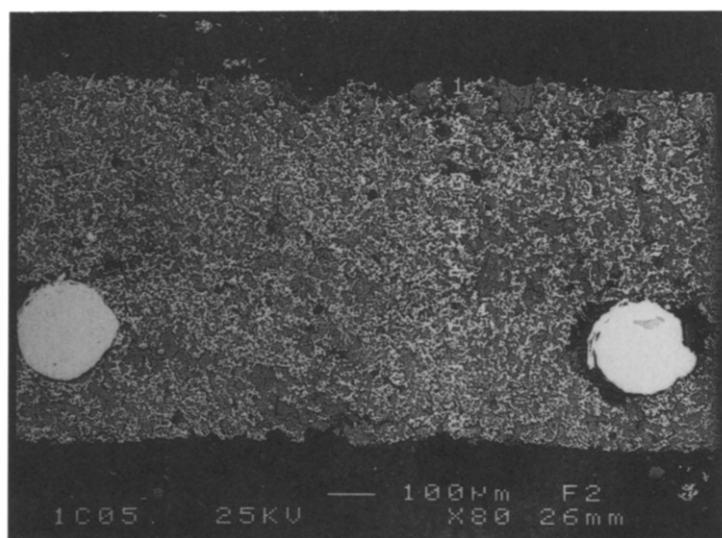
Sample 11: 1.82 M in Ni²⁺, 0.18 M Co²⁺ and 0.15 M Cd²⁺.

^bConcentration: g of metal in the active material/g electrode without screen.

^cNote: Iron is an impurity.



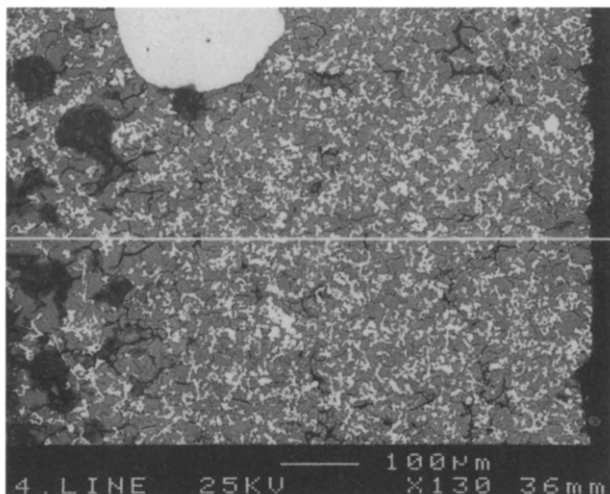
(a)



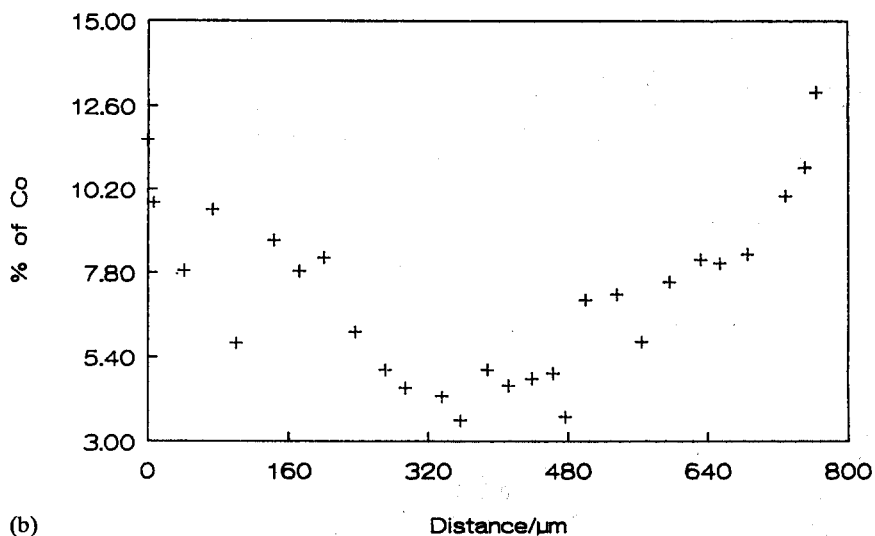
(b)

Fig. 2. Backscatter electron images ($\times 75$ to $\times 80$) of a typical area of the electrode cross section perpendicular to Ni screen: (a) before cycling, and (b) after cycling.

represent the Ni metal particles of the sintered substrate. Grey areas represent the active material while dark areas represent epoxy-filled voids of the electrode. The micrographs show, qualitatively, the distribution of the active material and Ni particles across the body of the electrode. In general, the distribution of active material appears to be uniform along the orthogonal directions, but uneven along the thickness of the sample, with the grey content (active material) increasing as one moves from the



(a)



(b)

Fig. 3. (a) An SEM picture of the whole cross section of a Ni electrode with Co additive and (b) the corresponding Co distribution; after cycling.

center of the electrode to the top (and bottom) surfaces. Upon cycling, the areas representing the active material show a visible increase. The probable reason is that the extended cycling causes a conditioning and activation of NiOOH.

Distribution of elemental components in the active material

In the previous section, the distribution of active material in the electrode structure, as examined by the SEM technique, was discussed. The analysis, however, does not give a complete description of the distribution of the elemental constituents in the

active material. To do this, two types of component distribution were considered: (i) across the entire thickness of the electrode, and (ii) between two sintered Ni particles at different portions along the thickness of the electrode. Figure 3 is an illustration of the analysis of the first type, using an electrode with Co additive only. The analysis was carried out on the grey areas only along the solid line shown in the micrograph of Fig. 3. The distribution shows a lower Co content at the geometric center of the electrode, and the content increases from the center towards the surfaces of the electrode. A semi-quantitative statistical analysis of the percentage Co distribution along the electrode sample often yielded average values which are comparable to the percentage Co content in the impregnation solution, and thus in the electrode. In the case of Fig. 3, the average value of the Co in the active material was around 7% while the reported Co content during impregnation was 7%. Figure 4 illustrates identical analysis for a typical electrode with both Co and Cd additives. The electrode sample for the latter case was prepared in an impregnation bath solution containing Ni, Co and Cd nitrates, with the composition based on the material added, in %, (93:4.2:2.6). In this Figure, R refers to the Ni:O ratio, a constant value of which would indicate an exact measure of the true elemental contents, as will be discussed later. The distributions of both Co and Cd are lower in the middle of the electrode than near the surfaces of the electrode in both cases, while the Ni:O ratio was constant within experimental errors. The observed higher concentrations of the additives at the surface than in the bulk might be due to preferential deposition of the additive ions relative to Ni ions in the impregnation bath conditions.

The second type of analysis is pictorially illustrated in the micrograph of Fig. 5. Here, the distribution of active components in the electrode is measured between two sintered Ni particles at microscopic points along a line which connects the two Ni particles. The analyses were performed at different positions along the thickness of the electrodes, for example, at the center between two Ni wires and also near the surface of the electrode. Flat distributions of the additives were observed for both

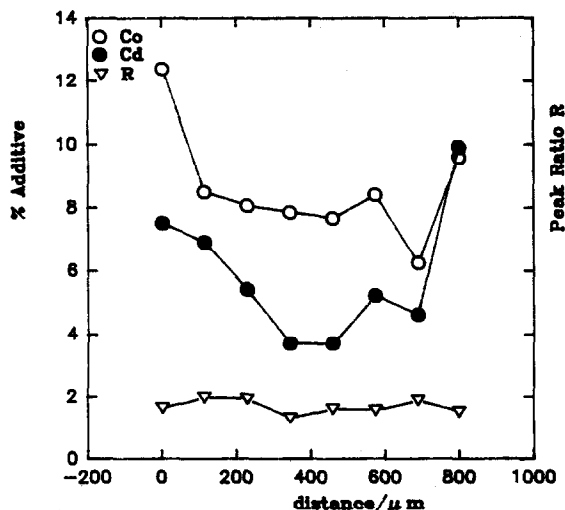
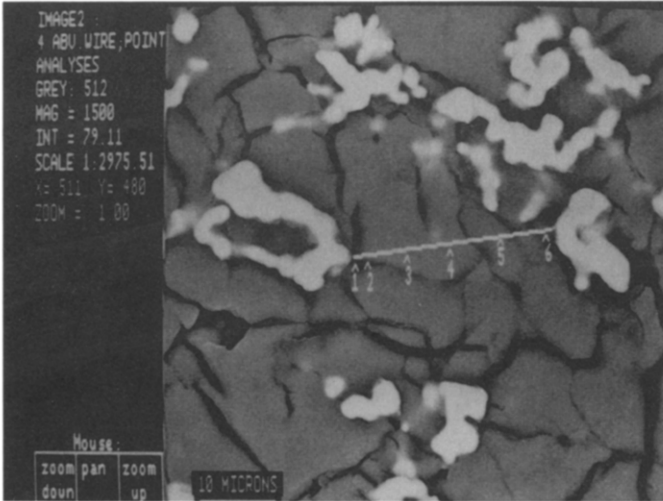
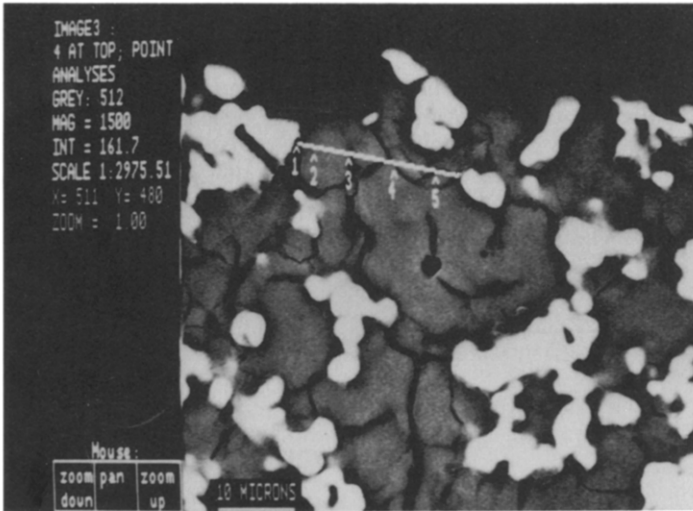


Fig. 4. Cross-sectional distributions of Co, Cd, and Ni:O ratios for an electrode with both Co and Cd additives; before cycling.



(a)



(b)

Fig. 5. SEM micrographs of an electrode showing locations of EDX analytical points for analysis of component distribution between adjacent nickel particles: (a) center portion, and (b) near surface; cycled electrode.

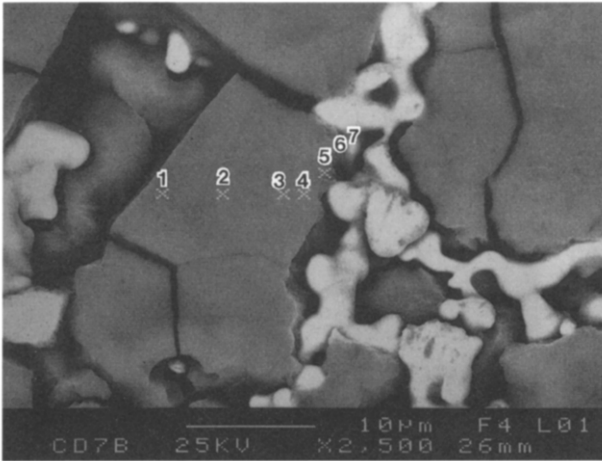
the electrodes with Co only, and Co and Cd additives. In other words, the additive (Co and Cd) content was found to be constant between adjacent Ni particles. Table 2 illustrates this trend in 'as-prepared' electrodes with 7 and 10% Co only additive for measurements carried out at analytical points near the surface, and at the center, of the electrodes. The flat micro-distribution of Co between adjacent Ni metal particles is consistent with results reported earlier [11, 12].

TABLE 2

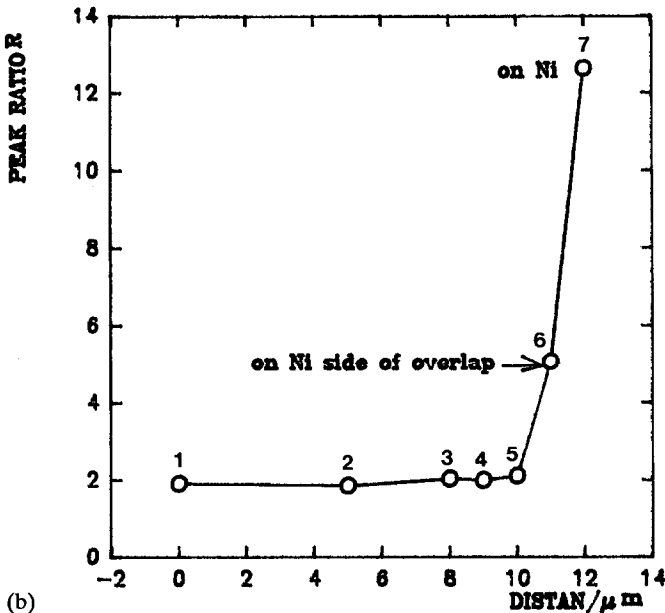
Results of EDX elemental analysis of active material in nickel electrodes which were prepared in an impregnation bath solution containing nickel and cobalt nitrates in ratios of (A) 93:7 and (B) 9:1, respectively

Electrode	Location	Micro-spots	Cobalt (%)	Nickel (%)	Potassium (%)	
A	Center	1	2.57	95.98	1.75	
		2	2.32	95.88	1.80	
		3	3.83	94.76	1.41	
		4	2.55	95.86	1.59	
		5	3.98	94.35	1.67	
		6	0.91	98.93	0.16	
	Near surface	1	9.36	89.3	1.34	
		2	8.65	89.94	1.40	
		3	8.52	90.18	1.29	
		4	9.64	89.05	1.32	
		5	8.25	90.44	1.31	
	B	Center	1	10.47	87.66	1.88
			2	11.88	85.64	2.48
			3	11.88	84.76	3.69
			4	11.74	84.48	3.78
5			3.60	95.37	1.02	
Near surface		1	13.88	81.98	4.14	
		2	12.77	84.37	2.86	
		3	13.43	83.43	3.14	
		4	2.99	96.25	0.27	
		5	7.89	90.44	1.66	

It has been argued that analyses based on SEM/EDX techniques are not sufficient to conclusively quantify the distribution of active components in a NiOOH electrode structure. This argument was based on the presumption that pure Ni particles from the sintered Ni and/or Ni screen current collectors may be exposed to the electron beam during the analysis, and thus the measured percentage would not give a true representation of the additives present. In this work, however, this problem has been overcome by measuring the relationship between the Ni_L and O_K peaks for each analytical point. A constant value from this relationship would indicate that the Ni analyzed was coming from the active material, rather than from Ni metal. In other words, a constant Ni_L:O_K peak ratio would indicate a negligible, if any, contribution of Ni from the screen and/or sintered Ni, or even more accurately, a uniform contribution to the total counts. To demonstrate the validity of this claim, an attempt was made to artificially increase this ratio by intentionally choosing analytical points close to a sintered Ni particle. This is illustrated in Fig. 6, and it can be seen that the peak ratio increased about sixfold when the analytical point was centered on a Ni particle. Otherwise, the peak ratio was constant in the grey regions of the micrograph representing the active electrode material up to the point where the beam was significantly less than 1 μm away from an exposed sintered grain. In the analyses described in the previous sections of this work, care was taken to only include analytical points for which the Ni_L:O_K peak ratios were constant. This way, only the contribution of the



(a)



(b)

Fig. 6. (a) An expanded view ($\times 2500$) of the electrode cross section showing locations of EDX analytical points. (b) Corresponding values of Ni:O ratios for same analytical points; cycled electrode.

active components in the electrode structure are taken into account for the determination of the distribution of the additives, and erroneous results due to the presence of shallowly buried sintered Ni could be avoided.

Using this technique, it should be possible to draw a correlation between the active material utilization (after cycling) and the electrode thickness. Such a correlation will be most beneficial in improving the Ni electrode performance.

Conclusions

This work has demonstrated the use of the SEM/EDX techniques to identify elements in a NiOOH electrode while simultaneously monitoring the distribution of both the active electrode material and the individual elemental components in the electrode structure. This was achieved by evaluating the Ni:O peak heights at each analytical point, a process which accounts for the validity of the measured percentages of the active ingredients in the electrode material. For the electrodes examined in this work, the distribution of the active material was found to be uneven across the thickness of the electrode, decreasing from the top and bottom surfaces towards the center of the electrode. Consequently, the individual element additives such as Co and Cd also decrease, following the same trend. However, at any analytical area along either orthogonal direction, the distribution of the elements remains constant between any two sintered Ni points.

Acknowledgements

The authors would like to thank Mr Joseph Stockel of the US Government his encouragement of, and useful discussions during, this work. Financial support by the US Government through subcontract P3-815300-U60 from Hughes Aircraft Company is also gratefully appreciated. Dr A. Visintin was at Texas A&M University on an international exchange program partially sponsored by CONICET-NSF.

References

- 1 D.F. Pickett, H.H. Rogers, L.A. Tinker, C.A. Bleser, J.M. Hill and J.S. Meador, *Proc. 15th Intersociety Energy Conversion Engineering Conf., Seattle, WA, USA, Aug. 18-22, 1980*, p. 1918.
- 2 J.L. Weininger, in R.G. Gunther and S. Gross (eds.), *Proc. Symp. The Nickel Electrode, Denver, CO, USA, Oct. 11-16, 1981*, The Electrochemical Society, Pennington, NJ, USA, pp. 1-18.
- 3 R.D. Armstrong, G.D. Briggs and E.A. Charles, *J. Appl. Electrochem.*, 18 (1988) 215.
- 4 H. Yasuda, *Denchi Toronkai*, 18 (1979) 89.
- 5 S. Januszkiewicz, *Proc. 13th Annual Power Sources Conf., Atlantic City, NJ, USA, 1959*, p. 75.
- 6 A.H. Zimmerman and P.K. Effa, *Proc. 19th Intersociety Energy Conversion Engineering Conf., San Francisco, CA, USA, 1984*, p. 169.
- 7 D.F. Pickett and J.T. Maloy, *J. Electrochem. Soc.*, 125 (1978) 1026.
- 8 M. Oshitani, Y. Sasaki and K. Takashima, *J. Power Sources*, 12 (1984) 219.
- 9 A. Visintin, A. Anani, S. Srinivasan and A.J. Appleby and H. Lim, in D.A. Corrigan and S. Srinivasan (eds.), *Proc. Symp. Hydrogen Storage, Materials, Batteries, and Electrochemistry, The Electrochemical Society, Pennington, NJ, Proc. Vol. 92-5, 1992*, p. 319.
- 10 A. Visintin, A. Anani, S. Srinivasan, A.J. Appleby and H. Lim, *J. Appl. Electrochem.*, in press.
- 11 A.H. Zimmerman, *J. Electrochem. Soc.*, 137 (1990) 2662.
- 12 H.S. Lim and S.A. Verzwylt, *Proc. 25th Intersociety Energy Conversion Engineering Conf., Aug. 1990*, Vol. 3, p. 7.