A LIGHTWEIGHT NICKEL COMPOSITE ELECTRODE
I: CONCEPT AND FEASIBILITY

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Summary

Composite metal–matrix materials, successful in various structural component applications, have not been widely employed to solve electrochemical energy storage problems.

The electrical efficiency, durability, and relatively high energy density of alkaline battery systems makes development of an improved sintered nickel electrode advantageous. Modification of current fabrication methods, however, should be targeted at a lightweight, long-life, low cost product, to be of any significant value.

The nickel composite electrode (Ni.C.E.) is fabricated by coating a graphite mat fiber material with a thin (0.6 - 1.0 μm) nickel layer and sintering to a compact structure. The resulting lightweight, durable composite structure is producible in porosities of 55 to >90%. This porous structure has been impregnated electrochemically with active material to a level of 200 A h/kg.

Test cells, containing single composite positives coupled with commercial negatives, exhibited lives approaching 800 cycles under a demanding cycling regime. The composite nickel electrodes showed utilizable gravimetric energy densities of 125 - 175 A h/kg under the test conditions.

The composite electrodes in multi-plate cells cycled under similar conditions had good capacity retention for 500 or more cycles. A gravimetric energy density of 120 - 125 A h/kg was noted for the entire positive plate block assembly including terminal. This is an increase of 66 - 72% over that measured for commercial positives. Volumetric energy densities for the Ni.C.E. are roughly equivalent to those of powder sinters. No detrimental effects due to the presence of graphite have been noted. Further optimization of this system may produce electrodes of still higher energy density.

Résumé

Des matériaux composés de métal–matrix, utilisés avec succès dans des applications structruales, n'ont pas été souvent employés pour résoudre des problèmes d'accumulation de l'énergie électrochimique

L'efficacité électrique, la durabilité et la densité relativement élévée d'énergie des systèmes de batterie alcaline rendant avantageux le développement d'une électrode perfectionnée de nickel frit (sintered). Cependant, toute modification des méthodes courantes de fabrication doivent tendre à développer une batterie (product) légère, de longue durée et bon marché, pour être de quelque valeur

L'électrode composée de nickel (Ni.C.E.) est fabriquée en enduisant (coating) un matériel de graphite (mat fiber) avec une couche mince (0 6 - 0.1 μm) de nickel et en la frittant (sintering) à une structure compacte La structure légère, durable et composée qui en résulte peut être produite en porosités (porosities) de 55 à >90% Cette structure poreuse a été imprégnée électrochimiquement de matériel actif à un niveau de 200 A h/kg

Des éléments d'essai, qui contiennent des positives uniques composées qui sont jointes à des négatifs commerciaux, ont démontré des cycles de vie qui approchent 800 cycles sous un régime cyclique exigeant. Dans les conditions d'essai, les électrodes composées de nickel ont démontré des densités d'énergie gravimétrique capables d'être utilisées de 125 - 175 A h/kg.

Les électrodes composées d'éléments de plaques multiples cyclées (cycled) et dans des conditions semblables ont manifesté la capacité de rétention de 500 cycles ou plus. On a remarqué une densité de 120 - 125 A h/kg gravimétrique d'énergie pour l'entière assemblée (plate block) positive comprenant la borne (terminal). C'est une augmentation de 66 - 72% par rapport à celle mésurée pour des positives commerciales Les densités de volumes (volumetric) d'énergie pour le Ni.C E sont approximativement égales à celles des sintages (sinters) en poudre. Aucun effet nuisible dû à la présence de graphite n'a été noté. L'amélioration additionnelle de ce système pourrait produire des électrodes d'une densité d'énergie encore plus élévée.

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1. Introduction

Fairly intensive research [1 - 3] has been concentrated on improvement of the sintered nickel electrode first developed in the 1930s and currently used in Ni–Cd, Ni–Zn, Ni–H$_2$, and other commercial and experimental battery and fuel cell systems. Some efforts have focussed on increasing the porosity of powder sinters while attempting to maintain acceptable structural integrity and electrical conductivity. Other research has sought to impregnate the powder sintered substrate more efficiently with the active material and increase its electrochemical utilization. While the powder sintered substrates have proven to produce durable and stable electrodes, several drawbacks remain: structural weight and high overall fabrication costs. Further attempts at improvement of the sintered electrode, therefore, should be targeted at a light-weight, long-life, low-cost product, to be of any significant value.

Significant progress has been made in recent years on metal–matrix composites for structural components where high strength and reduced weight are important factors. These composites have not been applied to solve the electrochemical energy storage problem to any great degree. This paper presents a feasible application of composite materials to an alkaline electrode structure.

The composite sintered electrode is a novel concept in which randomly interwoven nickel-coated-graphite fibers of inherently high tensile strength are sintered under compression to form a highly porous conductive medium [4, 5]. This is in contrast to the powder sintered material which depends upon bonded particulate chains for their strength and conductivity. Differences in geometry and physical properties of this composite substrate, as opposed to those encountered in previous sintered electrode studies, require that the procedures and results reported here be considered as evolutionary. Further optimization of the composite plaque and impregnation conditions is possible, subject to microscopic investigations and closer process parameter control.

2. Nickel composite electrode (Ni.C.E.) fabrication

Fabrication of the sintered Ni.C.E. takes place in three major steps:
(a) nickel coating of graphite mats;
(b) compression and sintering,
(c) impregnation/formation of active material.

2 1 The mat fiber
The Graphite Fibers ("Thornel" pitch mat, Union Carbide Corporation) used in fabricating the Ni.C.E. are highly graphitized, having a density of 1.9 - 2.0 g/cm^3. Their high density minimizes electrolyte infiltration into the individual fibers over time. Portions of uncoated fiber mat and several sintered composite plaques immersed in 31% KOH electrolyte at 75 °C for several months showed no signs of deterioration. Therefore, the mechanism of electrode swelling/failure due to fiber attack by the electrolyte appears to be negligible.

The graphite fiber mat product is a relatively inexpensive material intended for structural and insulative uses. Fiber diameters range from ~5 to 17 μm, a condition which inevitably leads to a less than ideal pore size distribution in the Ni.C.E. plaques. Data presented below confirm the breadth of this distribution. Graphite fiber materials uniformly coated with nickel by other than electroless methods are becoming available. These will be included in future studies of alternative Ni.C.E. plaque production techniques.

2.2 Nickel coating of the graphite fiber mats
A two-component electroless nickel plating solution (Allied-Kelite Division, Richardson Chemical Company) has been used exclusively to

produce the nickel plating for all test plaques. This method has been used principally because of its ready applicability to a beaker level operation. It does not necessarily produce either an expensive or best quality nickel coating for our purposes. The electroless coating contains 3 - 10% phosphorus by weight in addition to traces of the platinum catalyst material. These impurities do not appear detrimental to the production of good quality plaques. The chemistry of the electroless coating process is described quite adequately in the literature [6]. Good results in coating the graphite mats were achieved by following manufacturers' prescriptions for the coating of non-metallic surfaces

2 3 The sintering process

Sintering is a process which produces micro-welding of particles of certain metals heated in inert or reducing atmospheres The range of sintering temperatures is well below the actual melting temperature. Bonding in solid state sintering involves diffusion of atoms in the solid and/or vapor phase across particle interfaces. Sintering is used where an integral porous mass is desired. These masses can exhibit an accessible surface area several hundred times their outer surface area This property led to its application to the nickel electrode in the 1930s soon after the process itself was discovered.
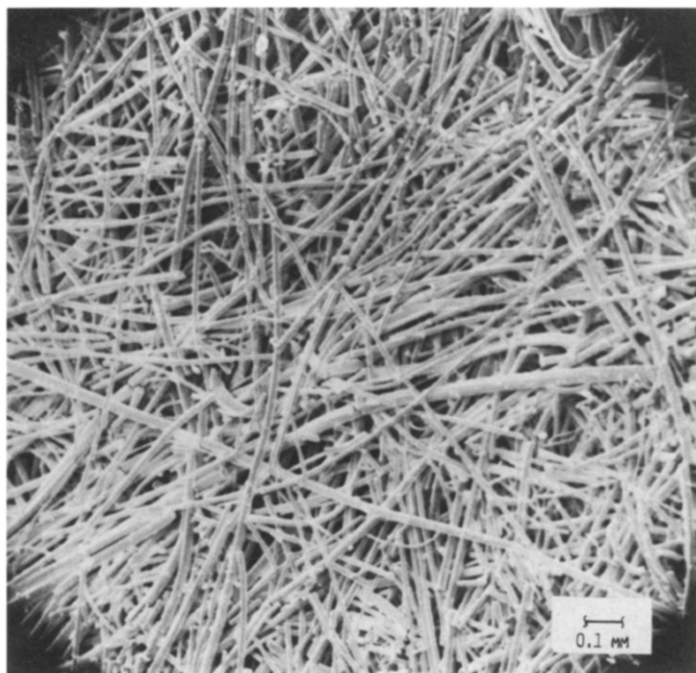

Fig 1 Composite sintered plaque micrographs Reproduced with the kind permission of The Electrochemical Society, Inc , from W A Ferrando and R A Sutula, Cycle life characteristics of composite nickel electrodes, *Proc Symp on the Nickel Electrode*, The Electrochemical Society, Inc , Pennington, NJ, Vol 82-4, 1982, pp 276 - 285
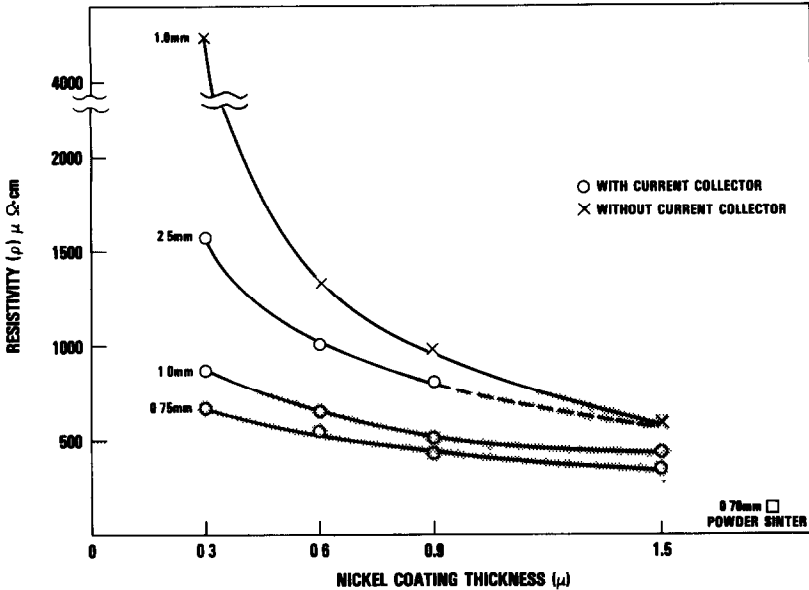
Fig 2 Electrical resistivity *vs* nickel coating thickness for various composite plaque thicknesses

Up to the present, most sintering has been carried out using fine, pure powders. This being the case, it was not at all clear that metal-coated fibers could be sintered because of their difference in geometry. We found, however, that the fiber mats readily sinter, under compression, in dry H_2 atmosphere at 800 °C. Our test plaques were formed by compressing several coated mats around a pure, expanded nickel mesh current collector. Typically, for a 40 mil thick plaque, 6 in. × 2.75 in., 2.5 grams of graphite mat (~7.5 g coated weight with a 0.6 μm nickel coating) yields a sintered plaque of about 85% porosity. A portion of such a plaque is shown in Fig. 1. A two hour sintering period was employed, although 15 - 30 min would be sufficient. Wet weights were taken prior to air drying followed by dry weight measurements. The porosity was determined in each case using the plaque volume and the volume of the imbibed water.

Resistivity measurements were made using a four point probe at several positions on the plaque surface. Typical resistivities lie in the range 200 - 600 $\mu\Omega$ cm. These values overlap those common to commercial powder sinters, as shown in Fig. 2 for plaques of various thicknesses.

Porosimetry measurements on a Ni.C.E. plaque have confirmed previous visual observations of a large pore size distribution and average pore diameter, due, in large part, to fiber geometry and to a lesser extent to the variation in fiber diameter. Mean pore diameters of 50 - 60 μm were computed from the data on plaques having fiber coatings of 0.3 - 1.5 μm nickel, respectively. Figure 3(A) and (B) compares the results of mercury porosimeter measurements on a powder sinter with a typical Ni.C.E. plaque. Further discussion on this topic is contained in ref. 7.
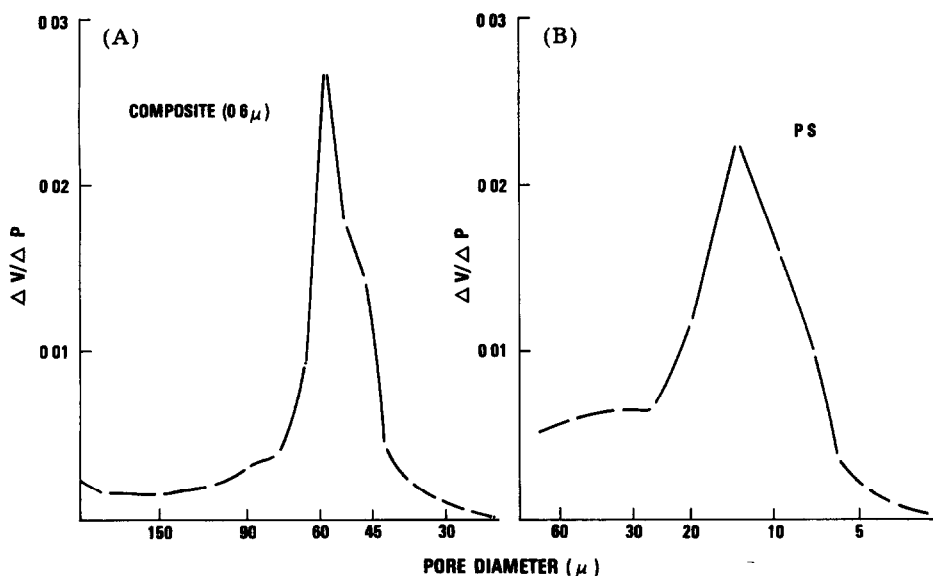
Fig 3 Mean pore diameter spectra (A) Composite plaque, (B) powder sinter plaque by mercury porosimetry

2 4 Impregnation of the sintered plaque

During the past twenty years, electrochemical methods [7, 8] of active material impregnation have been developed. The general feature of these methods is the use of an electrical potential to move Ni^{2+} ions from the bulk nickel nitrate solution into the plaque pores where simultaneous production of hydroxyl (OH^-) ions enables the active $Ni(OH)_2$ to be precipitated directly, eliminating the conversion step of the vacuum impregnation process. The prospect of higher active material loadings and the potentially simplified procedure have spurred much interest in electrochemical impregnation.

Except for a few electrodes made for comparison, all Ni.C.E. have been impregnated using the electrochemical method. Impregnation was carried out using a current regulated d.c. power supply, temperature controlled bath, nickel counter-electrodes, and appropriate nickel nitrate impregnation solutions. The particular impregnation method employed has been developed and described by Pickett [8]. The impregnating solution consisted of 1.8M nickel nitrate, and 0.135M cobalt nitrate in a 50 - 50 mixture of ethanol in water. Solution pH was returned to about 3.5 with dilute HNO_3 after each impregnation. During impregnation the pH was found to rise rapidly above 5.0, causing nickel hydroxide to precipitate directly on the plaque surface from the bulk solution rather than inside the plaque pores. Future studies will examine the effects of pH variation and will employ continuous control. The bath temperature was maintained at 75 - 80 °C.

After impregnation each electrode underwent five charge–discharge cycles ("formation"). This formation process involves alternate anodization

and cathodization in 20% KOH electrolyte. This treatment serves both to shed any loose, active material and to optimize that remaining within the pores The electrodes were washed in deionized water for several hours to remove any remaining traces of nitrate ions.

2 5 Test cells
Single plate
Test cells were constructed using commercial cadmium negatives of sufficient capacity to produce a positive limiting condition. A multi-wrap separator similar to that of a commercial cell was used. This consisted of a single layer of ion permeable membrane (Permion, RAI Research Corporation) sandwiched between two layers of a nylon woven material. Finally, the electrode assembly was placed in an electrolyte resistant, leak-tight, plastic case. A bubbler tube was employed to minimize electrolyte contamination by contact with atmospheric CO_2. A 31% KOH electrolyte was used with no additives. The electrode assembly was shimmed to fit into the case snugly, but was not compressed. Sufficient excess electrolyte was present for flooded conditions.

Multi-plate
A series of five multi-plate test cells was produced. Each positive Ni.C.E. was fabricated as described above. The plaque quality was substantially the same as in previous tests. Imperfections and blisters were evident on some plaques, especially after formation. Their cause was inadequate nickel plating on portions of some individual fiber mats used in the sintering due to insufficient agitation while in the electroless plating solution. The imperfections do not represent failure of the sintering process. As the nickel plating technique was improved, plaques of good quality and integrity resulted. An automated nickel plating process will be necessary to ensure consistent plaque quality.

The best of nine sintering runs (54 plaques) was chosen. Care was taken during the impregnation/formation process to insure that the pH was returned, using dilute nitric acid, to about 3.5 after each impregnation. While this procedure yielded improved results, manual adjustment of the pH was still not adequate to eliminate surface deposition and precipitation of the undesirable hydrated form of nickel hydroxide. Dynamic pH control is necessary to produce a compact, clean deposition of active material.

Cobalt additive concentration was maintained at 7% in the impregnation bath by weighing the nickel counterelectrodes before and after each impregnation and adding an appropriate quantity of cobalt nitrate prior to the following impregnation. Spectrophotometric concentration measurements of the impregnation bath verified the validity of this approach. Impregnation current density was set at 0.35 A/in.^{2} (0.054 A/cm^2), temperature at 75 °C. The electrodes were formed immediately in a 20% KOH solution after removal from the impregnation bath. This operation was carried out according to a seven step procedure. In successive 20 minute cathodization
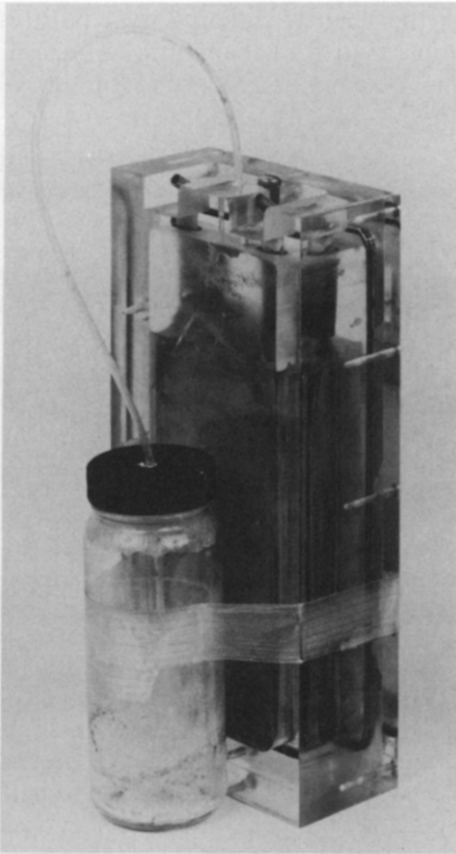
Fig 4 Multiplate test cell

and anodization cycles, current densities of 0.070, 0.031 and 0.011 A/cm^2 were applied. Finally, each electrode was washed for several hours in running, deionized water and soaked overnight.

After characterization, eight to eleven Ni.C.E. positive electrodes were interleaved with commercial negatives to complete the test cell shown in Fig. 4. Capacities were such that each cell was positive limited. The separator configuration was the same as that described for the single plate cells.

3. Results of cell tests and discussion

3 1 Life cycle data acquisition

In choosing a cycling regime for the tests, a compromise was made between overall cell stress (thermal, electrical, etc.) and the real time test completion requirements. The single plate cell tests consisted of repetitive constant current $C/2$ charge to 125% of capacity and 10 min open circuit rest, followed by discharge at $C/2$ constant current to 0.5 V cutoff. This is at least a 95% depth of discharge. This schedule was intermittently varied to
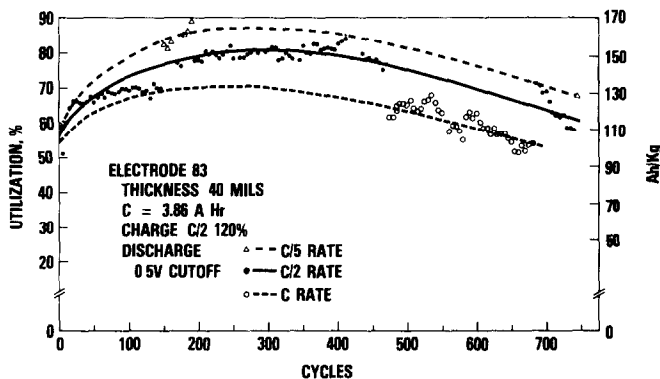
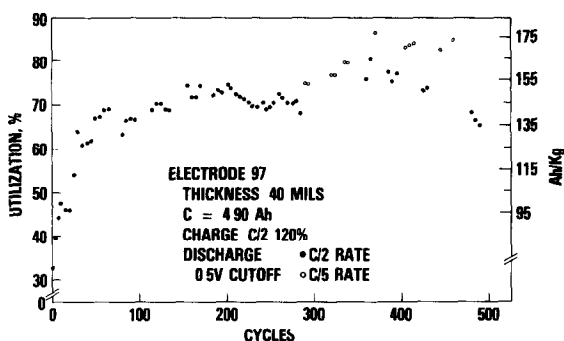Fig 5 Life cycle test data on single plate cell, electrode #83

Fig 6 Life cycle test data on single plate cell, electrode #97 Reproduced with the kind permission of The Electrochemical Society, Inc , from W A Ferrando and R A Sutula, Cycle life characteristics of composite nickel electrodes, *Proc Symp. on the Nickel Electrode*, The Electrochemical Society, Inc , Pennington, NJ, Vol 82-4, 1982, pp 276 - 285

include both C and $C/5$ rate discharges. C rating was determined from the weight gain of active material measured after formation using the nickel ion electrochemical equivalent of 0.289 A h/g. No special accounting was made for the cobalt additive in the active material, which was simply counted as nickel active material weight.

In the multi-plate cell tests, a charge rate of C was employed. This represents a rather demanding condition, especially considering internal heating of larger cells. It was assumed, however, that if the cells could meet life cycle requirements under these conditions, they could do so under less stringent conditions.

Figures 5 and 6 show typical cycle life test results on the single plate cells (1 positive Ni.C.E. plate, 2 commercial Cd negatives). The data exhibit common features. They each show a region of increasing utilization spanning the initial 80 - 150 cycles followed by a relatively constant plateau region extending to 500 cycles or so. Finally, there is a gradual performance decrease with further increase in number of cycles.

3 2. Analysis of single electrode cell data

In Fig. 5, various curves have been drawn through the data. These are intended to give an approximate indication of the cell lifetime at the discharge rates specified. Since these curves are based on a mixture of discharge rates for the same electrode, this interpretation of the data is only approximate. For an electrode discharged at the same rate throughout its life, lifetime is overestimated from the high rate (C) curve in Fig. 5 and underestimated from the low rate (C/5) curve. If cycling had been done simply at the low rate, the indicated lifetime for this rate certainly would have been greater. The reverse argument applies at the high rate.

The initial rise in utilization is most probably due to a rearrangement of the active material within the pores. Indication of this is shown in the scanning electron microscope photographs, Fig. 7(A) and (B). These are views of typical post-formation Ni.C.E. plates uncycled and heavily cycled (>200 high rate cycles), respectively. In the case of the uncycled plate, Fig. 7(A), the active material appears cracked and loosely bound to the plaque fibers. After heavy cycling, Fig. 7(B), the active material has been redistributed to closely adhere to the fiber surfaces. Isolated chunks of material have been replaced by a rounded, strata-like topology, indicating increased active material contact area. Distinguishable channels of electrolyte penetration are evident For rapid utilization increase, such an active material morphology must be present from the first few cycles. Cycling tests of Ni.C.E. plaque have shown that conversion of the sintered Ni to active material can account for no more than 7% of this rise [7].
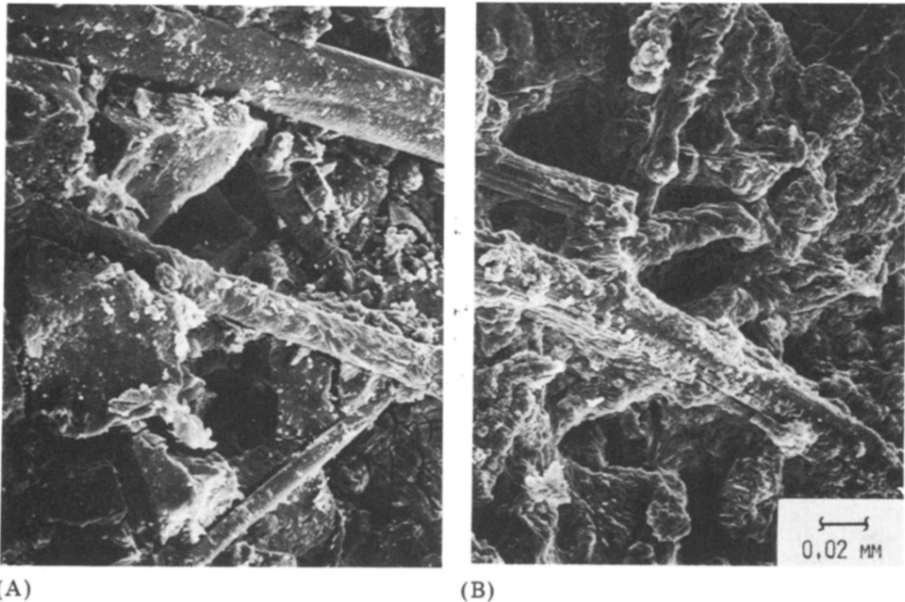

(A) (B)

Fig 7 Scanning electron micrographs of Ni C E surface (A) Post-formation uncycled (×300), (B) heavily cycled (×300)

TABLE 1

Electrolyte carbonate analysis*

Cell	Cycle	Discharge rate (A)	KOH (wt %)	mg CO_3^{2-}/ml KOH
0	0	0	27	Trace
50	82	0 2 C	22	Trace
54	296	2 C	34	Trace
57	211	3 C	32	Trace
Comm	> 400	Variable	—	170

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This period of rearrangement need not require many cycles, however, and is not a shortcoming of the Ni.C.E. plaque pore geometry. Our most recent results [7] show that a rapid rise (10 - 20 cycles) in utilization is attainable in Ni.C.E. plates up to 40 mil thick. This success has been achieved by adjusting the impregnation conditions to match the large average pore size of Ni.C.E. plaques more closely. The electrochemical impregnation method requires the simultaneous generation of hydroxyl ions at the pore walls and the entry of nickel ions from the bath into the pore in the proper concentration to produce a tightly packed mass of active material along the pore walls. Impregnation parameters (i e , current density, bath pH, bath concentration) found to be ideal for powder sintered nickel plaques must be modified for proper impregnation of the Ni.C.E. plaques. In turn, this will facilitate high utilization within a few cycles.

The gradual decrease in utilization from the plateau region in these data probably has several causes. The most important cause, probably, is the loss of electrical contact of active material due to cycling stress. The slight expansion and contraction of the active mass during cycling slowly detaches it from the current collecting structure (sintered Ni). Several other effects may be present. There is a possibility that some nickel hydroxide is converted to inactive nickel oxide. Sintered bonds can be broken also by slow conversion of the nickel coating to active material. Evidence for this is also presented in ref. 7. The resulting increased plaque resistivity would decrease utilization.

There was concern that the presence of a large quantity of graphite in an alkaline cell might cause carbonate contaminant to build up in the electrolyte. That this is not the case is shown in the wet chemical analyses (Table 1). (Modified titrimetric method by Margaret A. Reid, NASA Lewis Research Center, NASA Technical Memorandum 78961.)

The first entry is an electrolyte sample taken prior to insertion into the cells. The numbered entries show the results for electrolyte samples from cells cycled at moderate and high rates over a period of several months.

TABLE 2

Important nickel composite electrode physical characteristics

Electrode	Thickness (mil)	Loading (g/cm³ void)	Loading (A h/kg A h/lb)	Loading (A h/cm³ A h/in³)	C rating (A h)	Porosity (%)
54	24 0	1 49	123 9	0 252	1 65	71
			56 3	4 13		
59	19 7	1 66	132 6	0 349	1 9	75
			60 3	5 71		
61	19 0	1 62	139	0 355	1 9	71
			63 2	5 82		
83	42 4	1 49	189 8	0 383	3 9	89
			86 3	6 27		
85	42 0	1 66	191 4	0 408	4 3	85
			87 0	6 68		
97	43 5	1 98	204 6	0 41	4 9	82
			93 0	6 72		
101	44 0	1 88	168 6	0 375	4 8	71
			76 6	6 15		
Commercial manufactured 8/81	33 0	—	83 7	0 326	2 846	—
			38 1	5 34		

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On several cycles the cells were even reversed by accidental over-discharge. No carbonate was detected, however. An electrolyte sample from a commercial cell of undetermined history was included for comparison. Significant carbonate was detected in this sample.

Table 2 shows the important physical characteristics of positive plates in representative single plate cells. It is apparent from the entries that a rather high energy equivalent loading (A h/kg) of active material is possible for Ni.C.E. plaques of typical porosity. In fact, active material loading levels of 200 A h/kg are possible for porosities >85%. Calculation indicates that a loading level of 200 A h/kg requires the final electrode weight to be 3.25 times its initial plaque weight. While this is hardly possible to achieve with any powder sintered plaque, it can be accomplished with Ni.C.E. As the entry for electrode #97 shows, such a loading is possible without exceeding 2.0 g/cm³ void. Higher loadings than this are not normally used because of the tendency to produce premature electrode failure through swelling. It is not clear at this stage, however, whether utilizations approaching 100% will be possible in Ni.C.E. at such loading levels. Table 2 further shows that loadings on an electrode volume basis are comparable with those of the powder sinter. Typical loadings of 1.4 - 1.8 g/cm³ void produce theoretical gravimetric energy densities of 125 - 190 A h/kg.

TABLE 3

Nickel composite electrode single plate cell life cycle test data

Electrode	Discharge rate (C)	Cycle number	Utilization (%)	A h/kg	A h/cm^3
54	2	235	97	120 2	0 244
			86 4	107 0	0 218
57	3	100	94	112 4	0 199
			64	76 5	0 135
83	0 5	400	80 4	152 6	0 308
			71 8	136 3	0 275
	0 2	190	89 0	168 9	0 341
			86 6	164 4	0 332
	1	540	67 8	128 7	0 260
			43 0	81 6	0 165
97	0 2	450	82	170 0	0 340
			76	155 5	0 312
	0 5	470	75 5	154 5	0 310
			57 9	118 5	0 237
101	0 5	785	73 8	124 4	0 277
			66 9	112 8	0 251
	0 5	750	81 5	137 4	0 306
			77 4	130 5	0 290
	1	300	76 0	128 1	0 285
			60 0	101 2	0 225
Commercial	0 5	17	89 7	75 1	0 292
manufactured			87 8	73 5	0 286
8/81	1	5	90 8	76 0	0 296
			77 8	65 1	0 254

Table 3 presents typical performance data on electrodes in these single plate cells at various discharge rates and cycle number Several observations can be made

(i) At moderately high charge/discharge rates (C/5 - C/2) cell lifetimes are quite long, approaching 800 cycles. This indicates that at lower charge/discharge rates a cycle life in excess of 1000 can be expected.

(ii) At higher active material loading levels (1.8 - 2.0 g/cm^3 void), utilization tends to be reduced by 10 - 20% from those of moderate loading (1.4 - 1.6 g/cm^3 void). More thorough overnight rinsing of later test plates increased the observed utilizations by yielding more accurate values of active material weights. The heavily loaded plates still gave below 100% utilization, however. In these cases, the larger pores substantially filled with active material might not allow sufficient electrolyte or matrix surface contact for complete discharge. Microscopic studies in progress should help to determine the mechanism of poor utilization.

(iii) The performance of the Ni.C.E. positives on a gravimetric plate basis ranged from 125 to 175 A h/kg as compared with 75 - 110 A h/kg for commercial positives. Volumetric energy densities ranged from 0.25 to 0.34

A h/cm³ for Ni.C.E. compared with about 0 3 A h/cm³ for the commercial product.

The performance of Ni.C.E. noted in Table 3 should be considered as only the minimum possible. Important process variables, such as impregnation solution pH, were not well controlled. Impregnation current density was not optimized for the Ni.C.E. pore size A greater effort to control these variables was made during fabrication of the multiple cells. Even so, uncertainties in plaque coating quality and uniformity remained

3 3 Analysis of life cycle tests on multi-electrode cells

The cycling regime was chosen to provide a stringent cell test and to accumulate data quickly. This consisted of C rate charge to 125%, ten minutes open circuit rest, followed by C/2 discharge to 0.5 V. Figures 8 and 9 show the data obtained on two of these test cells. In each case, the scale to the right indicates the delivered discharge capacity in the form of the nickel
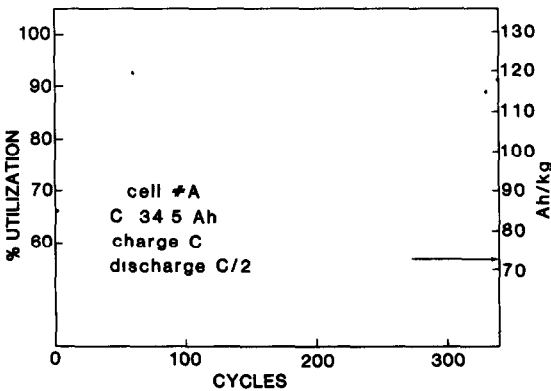

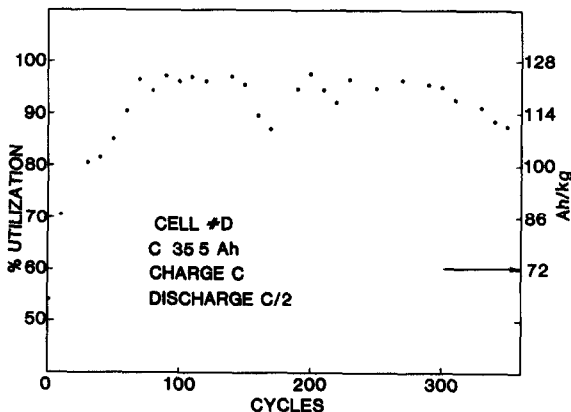Fig 8 Life cycle test data on multiplate cell A

Fig 9 Life cycle test data on multiplate cell D

TABLE 4

Multiplate test cell parameters for nickel composite electrodes

Cell number	Number of plates	Plate thickness (nominal) (in)	Average loading (g/cm³ void)	Average plaque (% void)	Utilization (plateau) (%) 0.5 V 0.9 V	Achieved* energy density (A h/kg)	Achieved* energy density (A h/cm³)	Cell rating C (A h)
A	10	0.40	1.285	80.8	94.5 - 86.5	121.5	0.249	34.5
B	11	0.30	1.11	83.3	96.0 - 90.0	106.0	0.213	24.9
C	10	0.20	0.99	81.4	95.0 - 93.0	77.4	0.210	13.8
D	8	0.40	1.639	82.7	85.0 - 71.0	121.1	0.305	35.5
E	8	0.30	1.57	82.7	102.5 - 86.5	125.2	0.321	23.4
Commercial	13	0.33	1.5 - 1.6	—	98.4 - 96.9	72.5	0.302	37.0

*Includes entire cathode plate block assembly, tab extensions and terminal (0.5 V cutoff)

electrode assembly gravimetric energy density (A h/kg) which includes the weight of terminal block and tabs. The arrow indicates the energy density measured for a typical commercial positive assembly, tested under similar conditions and compared on an equal basis.

As in the case of the single plate cells, common features include a slow rise in utilization to a constant or "plateau" value followed by a gradual decline with increasing number of cycles Possible mechanisms at work in the nickel composite electrode have been discussed above. Plateau utilizations of 90 - 95% were achieved after 40 - 80 cycles. Under the given test conditions, this plateau region extends to at least 350 cycles Table 4 summarizes the test cell results. The energy densities are based on the average plateau discharge capacities. Gravimetric energy densities in the range 120 - 125 A h/kg for Ni.C.E. compared, on an equal basis, with 72.5 A h/kg for the powder sinter, which is an improvement of 66 - 72%. Volumetric energy densities were in some cases comparable with cells containing powder sintered positives.

Table 4 also shows the positive electrode active material loading levels in g/cm^3 void and relative utilizations to 0.5 and 0.9 V cutoff cell potentials. There is a difference of several percent. in utilization at the $C/2$ discharge rate between the 0.9 and 0.5 V cutoff data which tend to increase slowly with cycle number. This is caused by the gradual rounding of the discharge curve "knee'. This, in turn, may be a consequence either of the presence of cobalt in the active material or simply of aging. Under the chosen cycling schedule, utilization begins to decrease after about 400 cycles. The causes of this deterioration in performance are considered to be basically the same as for the single electrode cells.

An additional mechanism of degradation which becomes important, especially in larger multi-plate cells, is the internal heat generation caused by the cell's internal electrical resistance. The electrolyte path length, separator, cell geometry, and plaque resistance all contribute to this internal energy loss. The results discussed above show an approximate two- to three-fold increase in plaque electrical resistivity for Ni.C.E. compared with that of powder sinter. A more uniform Ni coating will lower the resistivity of future Ni.C.E. plaques. Resistivities will remain somewhat higher than those of powder plaques, however. Therefore, attention to thermal management, especially in closely spaced, larger cells containing composite electrodes, will be necessary.

4. Conclusions

Fabrication and extended life cycle testing of single and multi-plate cells containing Ni.C.E. positives have demonstrated the feasibility of the composite plate concept for alkaline battery systems. Performance figures to date indicate a 66 - 72% gravimetric energy density improvement for the composite positives over present commercial positives at $C/2$ discharge rate.

Volumetric energy densities achieved by the composite test electrodes under conditions of high active material loading (>1.6 g/cm^3 void) are comparable with those of commercially available sintered nickel electrodes.

Full size Ni.C E. exhibit a gradual increase in utilization, followed by a plateau and gradual decline, observed to occur over about 600 cyles (C, $C/2$). Recent evidence indicates that the slow rise in utilization is due to mismatched impregnation/formation conditions and is not inherently a consequence of the peculiar Ni.C E. plaque morphology.

Control of nickel coating/plaque pore uniformity and impregnation/formation conditions are each important steps in the production of a long life, high energy density Ni.C E. Investigations continue on alternative methods of Ni.C E plaque production and on achieving optimal impregnation/formation conditions for these electrodes.

No carbonate contamination of the electrolyte in heavy cycling was detected by chemical analysis.

Relatively long electrode life under heavy cycling indicates good dimensional stability and active material adherence in the Ni.C E.

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