

ADVANCES IN LIGHTWEIGHT NICKEL ELECTRODE TECHNOLOGY

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Summary

Studies are currently underway to further the development of light-weight nickel electrode technology. Work is focussed primarily on the space nickel-hydrogen system and the nickel-iron system, but it is also applicable to the nickel-cadmium and nickel-zinc systems. The goal is to reduce electrode weight while maintaining or improving performance, thereby increasing electrode energy density. Two basic electrode structures are being investigated. The first is the traditional nickel sponge produced from sintered nickel carbonyl powder. The second is a new material for this application which consists of a non-woven mat of nickel fiber. Electrodes are being manufactured, tested, and evaluated at the electrode and cell level.

Introduction

Eagle-Picher has been involved in nickel electrode development for a number of years in association with many different battery systems. Our current work with the nickel-hydrogen system dates back to 1969 and has evolved from previous work with aerospace nickel-cadmium and zinc-air battery cells. The goal throughout has been to increase the energy density of the nickel positive electrode (and, hence, the battery) while maintaining a satisfactory level of performance. For space applications, performance includes sufficient useful life as well as cell electrical characteristics.

The goal of increasing cell energy density provided the original impetus for the development of the nickel-hydrogen system. Replacing the heavy cadmium negative electrode of the nickel-cadmium cell with a lightweight catalytic gas electrode provided a substantial saving in weight. Nickel-hydrogen cell designs have been continuously refined over the years to remove even more system weight. However, cell pressure vessels and structural components can be reduced in weight only to a finite degree due to safety considerations and launch dynamics requirements. Common pressure

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vessel battery designs hold some promise for further weight reductions but are not currently being used in production programs.

The best opportunity for further weight savings without serious deviation from existing flight cell designs would appear to lie in the electrochemically active cell components. The nickel electrodes account for about forty percent of the total finished weight of a current design, flight production, nickel-hydrogen cell. Therefore even a small increase in the energy density of the electrode would amount to a substantial benefit at the cell and battery level.

The nickel electrode consists of two basic components. These are the active material and the support matrix. Active material utilization has been optimized in past efforts and probably cannot be increased much past current levels. The most likely opportunity for weight reduction is in the structural matrix of the electrode which houses the active material. For conventional sintered nickel-carbonyl powder electrodes this would require producing a higher porosity matrix, a lighter weight current collector/substrate, or a thicker electrode. Use of a nonwoven mat of nickel fibers as an alternative lightweight, high porosity matrix is also being explored.

Sintered nickel carbonyl powder electrodes

The production of battery electrodes from sintered nickel carbonyl powder is a well established technology and has been extensively investigated and reviewed. However, work is still being done to refine the process further for high reliability, long life, and weight-critical applications. Two basic processes are currently in use to produce electrodes for the nickel-hydrogen system. One is a dry powder method in which each individual plaque is hand-laid in a mold, one at a time. The second is a wet slurry process in which the plaque is produced in a continuous roll. Both methods use a similar nickel wire mesh substrate and sintering process and yield a similar product.

Once the porous nickel matrix is obtained it must be loaded with active material to produce a working electrode. The chemical impregnation method used for many years to produce nickel-cadmium electrodes has been entirely replaced by an electrochemical process in the nickel-hydrogen system. Electrodes are produced in either an aqueous solution or an aqueous/alcohol solvent system. Both processes have the advantage of loading the active material in one impregnation step rather than in many repeated cycles, as in the chemical process. Other advantages of electrochemical impregnation include improved cycle life, utilization, and dimensional stability.

Electrodes produced by the wet slurry method and the dry powder method exhibit relative advantages to each other. Both processes are characterized by extensive quality control provisions (*e.g.*, strict, tight tolerance requirements from raw materials, operational process steps, and finished component testing) in recognition of their criticality to the finished product. The slurry process is a continuous-feed, more efficient, and less operator-dependent process. The current-collector substrate is automatically centered

in the electrode structure by the nature of the process. This provides electrical and structural benefits. The material has high mechanical strength in terms of both tensile and bend properties. Slurry-type plaque holds up to the rigors of electrode processing and handling, resulting in a low attrition rate during the multi-step production process. The slurry-type material better accepts attachment of electrical conductors by resistance welding without forming cracks in the heat-affected zone and surrounding sinter. Part of the slurry production process involves a wet oxidation step which covers the surface of the plaque with a thin passive oxide layer. This serves to provide a more durable product with low susceptibility to mechanical damage or chemical corrosion. Most importantly, slurry-type electrodes exhibit good dimensional stability and should provide a longer cycle life at higher depths-of-discharge.

Electrodes produced by the dry powder method possess inherent battery weight and energy density advantages. Dry-powder-process electrodes have a higher porosity structural matrix. This results in a higher active material to inactive substrate weight ratio and greater energy density. Dry powder electrodes are also manufactured with a greater electrode thickness. Increasing the thickness of the electrode has a net effect of increasing cell energy density by requiring fewer electrodes and associated cell components to achieve the same ampere-hour capacity.

Historically, applications of the space nickel-hydrogen system have been with slurry-type electrodes impregnated by the aqueous electrochemical method. This extensive data base has been reviewed previously [2] and includes five major satellite programs (18 launches total) which are currently operating in orbit with nickel-hydrogen batteries on board. The ideal electrode, therefore, would be one which combines the mechanical strength and dimensional stability of slurry-process plates with the higher porosity and greater electrode thickness associated with dry-powder-process plates.

Accordingly, manufacturing parameters were adjusted to produce several lots of 35 mil-thick slurry process plaque with porosities ranging up to 86%. These plaques retained 60 - 80% of the nominal mechanical strength of normal 80% porosity, 30 mil thickness slurry plaque. Each lot was impregnated and formed by normal manufacturing procedures, and two plates from each lot were subjected to a standard, flooded capacity measurement, and a 200 cycle stress test. All plates tested exhibited satisfactory utilization numbers in the 120 to 130% range. However, a growth *versus* porosity plot of the 200 cycle, 10 C stress test data (Fig. 1) shows that there is currently a breakover point at around 83% porosity beyond which the amount of electrode growth becomes excessive. Thickness growth is undesirable, as it has been previously identified as a major contributor to long term cycle failure of nickel-hydrogen cells [1].

Two lots with porosities of 82.7% and 84% were selected for further cycling. These plates underwent a total of 1000 stress test cycles with a visual inspection for physical integrity and growth measurements, conducted at the completion of 200, 600, and 1000 cycles. Flooded capacity tests were

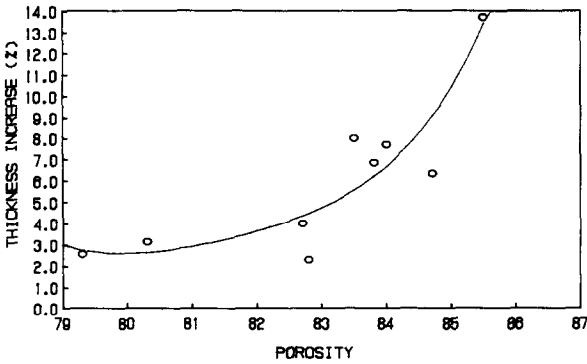


Fig. 1. Electrode growth vs. porosity: high porosity slurry.

run at the conclusion of each 200 cycle increment. None of the plates blistered or suffered a loss of capacity during the 1000 cycles of testing. Thickness increase peaked at 600 cycles for both lots. The 82.7% porosity lot exhibited less than 6% thickness increase after the completion of 1000 cycles.

Figure 2 shows the relationship between electrode growth and active material loading on a grams-per-cubic centimeter-of-void-volume basis. These 200 cycle 10 C stress test data suggest that the loading of high porosity slurry plates can be increased beyond current flight acceptable levels and thereby increase the energy density.

The goal of future development work is to push the breakover point demonstrated in Fig. 1 beyond 84% porosity through further refinement of slurry process manufacturing parameters. Impregnation and formation of these high porosity slurry plaques will take place in Eagle-Picher's new nickel-electrode production facility. This facility has been expressly designed and dedicated to the space nickel-hydrogen system. As noted above, in recognition of the criticality of the component, the facility was designed from the group up for full automated computer process control.

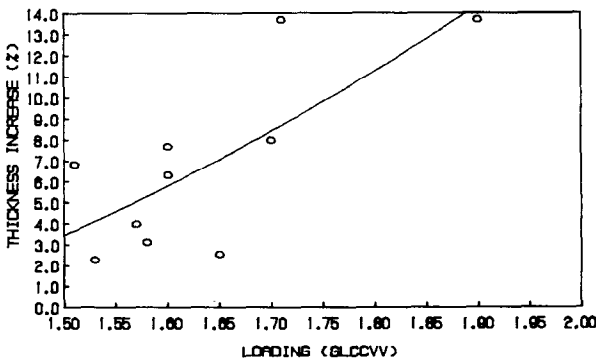


Fig. 2. Electrode growth vs. loading: high porosity slurry.

The generated process data form the basis for a quality control statistical analysis with "real-time" feed-back provisions offering continuous, detailed process control.

Improved tank flow characteristics, greater solution-volume to plaque-area ratios, automated cycling and pH control, an oil-cooled balancing resistor network for equal current distribution, and computerized monitoring and recording of production parameters, will allow tighter control and reproducibility of the manufacturing process. Slurry process electrodes with nominal porosities of 82% have already been produced in Eagle-Picher's existing facility, evaluated at the electrode level, and are currently being assembled into cells. It is anticipated that a nominal mass saving of approximately 10% will be achieved at the finished cell level.

Non-woven nickel fiber electrodes

Work has taken place over the last several years on a non-woven nickel fiber material as a possible replacement for conventional, sintered nickel powder type plaque. The material is manufactured by the National Standard Company under the trade name Fibrex (TM) and has received renewed interest recently. It has the potential for substantial improvements in energy density and material cost reduction. Some of the previous work with fiber mat had been unsuccessful because of problems in loading the active material and the resulting dimensional instability of the finished nickel electrode. The major problems appeared to be due to the open structure and large pore size of the mat and its lack of mechanical strength.

More recent work has been conducted mostly in relation to the nickel-iron battery system under the Dual Shaft Electric Propulsion (DSEP) Program funded by the United States Department of Energy (DOE). This investigation has been undertaken due to the development of a nickel fiber mat which has been cross-linked with battery grade nickel powder. This material has the potential for providing the necessary mechanical strength and dimensional stability required for long cycle life battery electrodes. Current work is focussed on adjusting the fiber-to-powder ratio and the sintering conditions to achieve an optimum electrode for a given cell design. Cross-sectional strengths have been increased by a factor of ten over the earlier materials. The fiber mat promises good performance and design versatility through close control of electrode parameters such as weight, strength, surface area, pore size, and thickness. A 12% saving in weight over the sintered powder electrode is realized, solely due to the elimination of the grid wire support/current collector structure not required by the mat. Further weight savings may be achieved from the higher porosities and active material loading obtainable from the fiber mat.

The problems associated with loading the active material into the fiber mat have been overcome, in part, by applying a periodic reverse impregnation process. The method is essentially the same as the normal aqueous

electrochemical process except that the polarity of the electrodes is periodically reversed during impregnation. Periodic current reversal is commonly used in the metal plating industry to promote a more uniform deposited film on the work piece. It appears to have a similar load leveling effect in impregnating nickel electrodes with active material. Work is underway to continue investigation of plating/deplating current densities and cycle times to achieve optimum results. This method has an additional benefit of yielding a 20% higher ampere-hour efficiency in loading the plate over the normal constant current process.

Nickel-iron cells have been constructed and tested using electrodes produced from a 50% fiber/50% powder nickel fiber mat. The porosity of the plates was 75%, the thickness 0.040 in., and the nickel fiber diameter 20 μm . The plates were impregnated through two cycles due to inadequate active material weight gain after the first cycle. After formation in aqueous potassium hydroxide the plates had an average active material loading of 1.54 g cm^{-3} of void volume. A plate was assembled into a test cell and 50 cycles were performed at 100% DOD (Fig. 3). On-going research is now exploring sinter porosities up to 85 - 90% which will offer specific energy advantages.

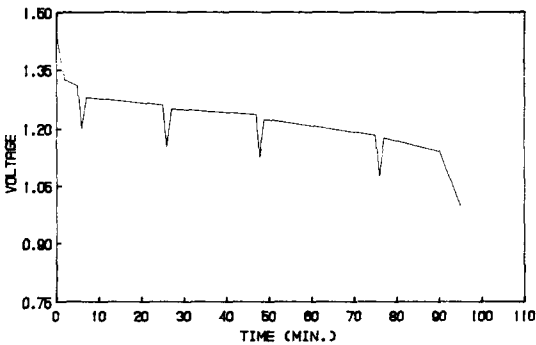


Fig. 3. Fiber electrode pulse rate test.

Additional testing was developed for use in the DSEP Program to determine the best electrode design for optimum power capabilities. The test is composed of a base discharge at a $C/2$ rate with 2.25 C -rate pulses at 95%, 75%, 50%, and 20% of the working capacity. Testing was performed on fiber electrodes (Fig. 4) with normal sintered electrodes as a control. It was concluded that the sinter electrode gives greater instant power within the first three pulses. However, the sinter electrode appears to increase in impedance over the discharge cycle more than the fiber electrode. The fiber electrode also yields a greater utilization of active material per gram than the sinter electrode. The fiber electrode could be developed to supply more power over the discharge curve by improving its dimensional stability. This would increase the contact area of the fibers, thus lowering the internal resistance of the plate.

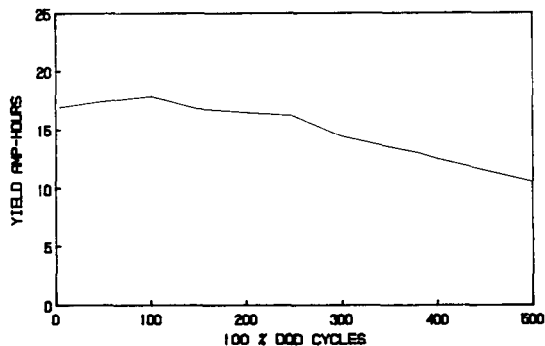


Fig. 4. Fiber electrode cycle test.

Further investigation into the utilization and electrochemical efficiency of the fiber electrode was made by Dr Alvin J. Salkind and Associates. This was accomplished by a subcontract from the base technology contract with DOE for the development of the nickel-iron battery.

Testing was performed comparing the rate capability of 0.063 in.-thick sintered- and fiber nickel plates at various states of charge (SOC), but the fiber-based plate supported higher current densities at the lower SOC of 25% (Figs. 5 and 6). The impregnation loading level of the fiber nickel plate was much lower than the standard sintered plate, with a consequent reduction of capacity.

The marked differences in scope, and ability to sustain heavy loads at a low state of charge, may only be a consequence of the relatively low active material content of the fiber plate. However, it seems likely that the fiber material can be loaded higher and still perform as well as a sintered plate of comparable active material density.

Conclusions

Considerable progress has been made toward improving the nickel electrode for high reliability, long cycle life space applications. The goal has been to increase energy density while maintaining currently acceptable flight program active material loading levels. In addition, the goal has been to advance significantly the level of quality control provision implementation and the level of quality control process data utilization for enhanced, "real-time", total process control. Electrodes produced for early nickel-hydrogen flight cell programs had an average energy density of about 0.135 A h g^{-1} . Current flight production programs have achieved energy densities at the electrode level more than 20% greater than that value at the same active material loading on a g cm^{-3} of void volume basis. This translates into a substantial weight saving at the finished flight level.

Further increases should be attainable in the near future within the scope of current production technology. The main thrust of Eagle-Picher's

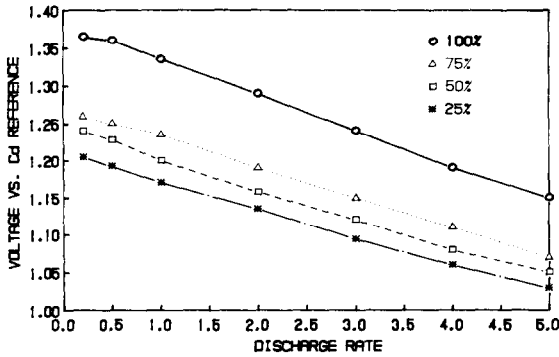


Fig. 5. Fiber nickel electrode. Voltage vs. discharge rate and state of charge.

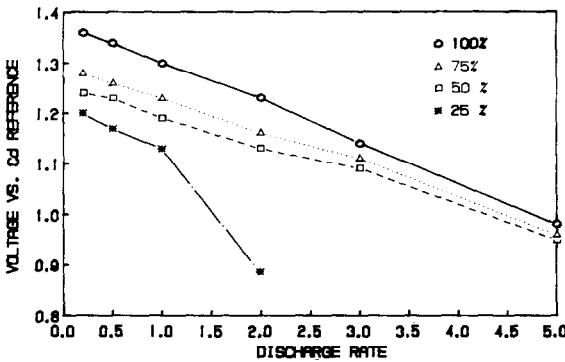


Fig. 6. Sintered nickel electrode. Voltage vs. discharge rate and state of charge.

future research work will be to develop a mechanically strong, thick, high porosity nickel electrode. Current data suggest that this electrode will more likely be produced using the wet slurry manufacturing process, but work will continue with both the slurry and dry powder processes.

Nickel fiber mat appears to be a promising replacement for the traditional nickel sinter substrate. Preliminary testing has shown it to be a viable battery electrode with distinct weight advantages. Work will be continued towards the further development of optimized fiber electrodes for nickel battery systems.

In addition to superior physical performance and enhanced component quality, it is anticipated that both of the above electrode substrate materials will eventually result in overall system cost reductions.

Acknowledgements

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fiber electrode work. Much of the early basic testing and evaluation work on nickel sinter was performed by the Communication Satellite Corporation Laboratories, funded by the International Telecommunications Satellite Organization.

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