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(NASA-TM-X-71556) PREDICTED ENERGY DENSITITES FOR NICKEL-HYDROGEN AND SILVER-HYDROGEN CELLS EMBODYING METALLIC HYDRIDES FOR HYDROGEN STORAGE (NASA) ~~11~~ p HC $3.00 CSCL 10A G3/03

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Summary

Simplified design concepts were used to estimate gravimetric and volumetric energy densities for metal-hydrogen battery cells for the purpose of (1) assessing the characteristics of cells containing metal hydrides as compared to gaseous storage cells, and (2) comparing nickel cathode and silver cathode systems.

The silver cathode was found to yield superior energy densities in all cases considered.

The inclusion of hydride forming materials yields cells with very high volumetric energy densities that also retain gravimetric energy densities nearly as high as those of gaseous storage cells. Such hydride containing cells may also offer higher reliability and/or longer life by virtue of eliminating the high pressures and large pressure changes that must be withstood by gaseous storage cell containers.

Introduction

In the last few years considerable interest has been generated in metal-hydrogen secondary batteries, nickel-hydrogen in particular, and to a lesser extent silver-hydrogen. Metal-hydrogen batteries offer higher gravimetric energy densities (watt-hr/kilogram) than do the nickel-cadmium cells presently used in space applications, and the cycle life - of the nickel-hydrogen at least - is potentially comparable. Silver-hydrogen offers a substantial increase in gravimetric energy density relative to nickel-hydrogen but with considerably lower cycle lifetimes. Other attractive features of metal-hydrogen systems are deep discharge capability, insensitivity to over-charge and over-discharge, and the availability of the hydrogen pressure as a state-of-charge indicator.

Typical metal-hydrogen batteries incorporate gaseous hydrogen storage by allowing the hydrogen generated during charge to fill the interior of the cell container. Such a storage method, however, penalizes the battery from the standpoint of volumetric energy density (watt-hours/liter), and the high pressures required coupled with pressure cycling make container integrity a concern for long term applications.

The incorporation of a hydride forming metal or alloy offers an alternative to strictly gaseous storage, acting as a reservoir which "fills" during charge and "empties" during discharge, thereby minimizing both maximum pressure and pressure changes during cycling.

The study reported herein was undertaken to determine whether such hydride-containing cells are feasible or attractive from an energy density point of view. A secondary goal was the comparison of nickel-hydrogen and silver-hydrogen in the various configurations considered.

Approach

Gravimetric and volumetric energy densities were calculated for a number of 50 ampere hour total capacity metal-hydrogen cell designs. The basic configuration chosen (for computational ease) was circular flat plate cells stacked in a cylindrical container with hemispherical end caps, for gaseous storage, or dished heads with spherical radius twice the cylindrical radius for hydride reservoir systems. All can calculations were accomplished via thin wall container relationships.

The baseline design was gaseous storage nickel-hydrogen, which was "redesigned" for the other systems as necessary.

Baseline Gaseous Storage Nickel Hydrogen Design

The stacking sequence is shown in figure 1. Cell components are circular with a central axial passage for electrical leads, tierod and gas distribution. Edge gasketing was assumed for all components save the inside edge of the gas spacer screen. The cathode was assumed to be made up of two standard nickel electrodes back to back.

Figure 2 shows the stack and can configurations. The quantities used in the calculations are given in Table I.

The calculational scheme used yields stack radius, thickness, and weight as a function of number of subcells. The current density is found to be a function only of the cathode fixed parameters, the depth of discharge (100 percent in these calculations), and the discharge period (taken as 1 hr).

The inner can radius is equal to the stack radius. The can length determines the amount of gas storage volume available, which with the precharge pressure determines the maximum pressure and hence the required can wall thickness.

The minimum volume cell for a given stack radius clearly is obtained by making the can just long enough to contain the stack. The minimum weight can for most stack radii is, however, somewhat longer. The optimum length (with respect to can weight) of the cylindrical portion of the can is given by

$$L_{\text{optimum}} = \delta_s + \frac{4}{3}r\left[\sqrt{\frac{3}{16}\,\frac{CRT}{\pi r^3 P_0 e_{H_2}}\left(1 + \frac{3}{2}\,\frac{\delta_s}{r}\right)} - 1\right]$$

where δ_s = stack thickness, r = stack radius, C = total stack amp-hour capacity, R = gas constant, T = temperature, P_0 = precharge pressure, and e_{H_2} = specific capacity of hydrogen (26.8 amp-hr/gram).

This optimum results from the fact that as the can length increases, the maximum pressure - and thus the required wall thickness - decreases. But as the can length is increased beyond $L_{optimum}$ can dimensions become the weight controlling factor rather than wall thickness, and even though the maximum pressure continues to decrease, can weight begins to increase. Note that the optimum length depends on the initial or precharge pressure (P_0) chosen, and that $L_{optimum}$ diminishes to the stack thickness as precharge pressure or stack radius increase.

Gaseous Storage Silver-Hydrogen Design

Four somewhat different stack options were considered:

1. Identical to nickel-hydrogen stack excepting the substitution of back-to-back silver cathodes for the nickel cathodes.

2. Same as (1) excepting the substitution of interanode electrolyte reservoirs (I. E. R. S) for gas spacer screens (see discussion below).

3. Same as (1) with single silver cathodes instead of back to back.

4. Same as (2) with single cathodes rather than back to back.

Table II gives the quantities which differed from those of Table I.

The single silver cathode cases were considered because of the high current density associated with the back-to-back cathodes which results from the higher specific capacity of silver electrodes.

The silver-hydrogen system differs from nickel-hydrogen in that water is a stoichiometric participant in the cell reaction, which serves to complicate electrolyte management in silver-hydrogen cells. A technique that has been successful in alleviating electrolyte management problems in alkaline hydrogen-oxygen fuel cells is the inclusion of electrolyte reservoirs abutting each anode. Comparative calculations were therefore made for otherwise identical silver-hydrogen stacks with and without interanode electrolyte reservoirs (in cells without some type of reservoir, cathode volume changes would be relied on to balance electrolyte volume changes).

The I. E. R. S. were assumed to be sintered nickel plates with a pinfield impressed on each side to allow hydrogen flow across the faces of the adjacent anodes. One I. E. R. would replace each gas screen in the stack, and the thickness of each I. E. R. is given by:

$$\delta_{IER} = \frac{0.34\,\delta_c \rho_c e_c d}{\epsilon(1 - f)} + 2\delta_{PF}(1 - \alpha)$$

where 0.34 is the specific volume change (cm^3/amp-hr), δ_c = cathode thickness, ρ_c = cathode apparent density, e_c = cathode specific capacity, d = cathodic depth of discharge (100 percent in these calculations), ϵ = sinter porosity, f = fullness factor (i. e., the I. E. R. is chosen to be "f" full - 1/3, 1/4, etc. - at complete charge), δ_{PF} = pinfield height, and α = pinfield coverage fraction.

The general calculational procedure used for the gaseous storage silver hydrogen cells was the same as that described for the nickel hydrogen cells.

Hydride Reservoir Cell Design

Hydride reservoir systems were taken to consist of a gaseous storage type stack with circular disk hydride reservoirs added to the outer surface of each endplate. Hydrogen transfer would be accomplished by means of the stack axial passage. Cylindrical Inconel cans just large enough to accommodate the stack plus reservoir were capped with semi-spherical dished heads with inside radius equal to twice the can radius.

An approximate model of the reservoir/stack system dynamics was developed to aid in sizing the reservoir and determining the maximum pressure. Assuming isothermal operation, first order reversible hydride formation and decomposition kinetics and constant charge or discharge rate, the describing equations are

$$M \frac{dX}{dt} + \frac{V}{RT}\frac{dP}{dt} = S \tag{1}$$

$$\frac{dX}{dt} = k[P - P^*(x)] \tag{2}$$

where M = gram moles of hydride forming material, X = moles of hydrogen (H_2) as hydride per mole of hydride forming material, V = gas filled volume, R = gas constant, T = temperature, S = rate of hydrogen addition or removal via the electrochemical process, P = hydrogen pressure, $P^*(x)$ = the equilibrium pressure of hydrogen associated with a given mole ratio X, k = the first order hydride formation rate constant, and t = time.

Most hydrides exhibit equilibrium isotherms of the type shown in figure 3. Notice the two-phase or "plateau" region of the isotherm, bounded by X_1 and X_2 and characterized by the plateau pressure, P_P.

If the system described by equations (1) and (2) is initially in equilibrium and if X remains in the plateau region, equations (1) and (2) yield

$$X = X(0) + \frac{VS}{RTkM^2}\left(\frac{RTMkt}{V} - 1 + e^{-RTMkt/V}\right) \tag{3}$$

and

$$P = P_P + \frac{S}{kM}(1 - e^{-RTMkT/V}) \tag{4}$$

with

$$S = +0.0187\,\frac{C}{t_c} \qquad \text{during charge}$$

and

$$S = -0.0187 \frac{C}{t_D} \qquad \text{during discharge}$$

where 0.0187 is the gram-moles of hydrogen involved per amp-hour of charge or discharge, C is the total amp-hour capacity, t_C is the charge duration, and t_D the discharge duration.

The minimum amount of reservoir material necessary may be established by one of two limitations:

a. X at the end of the charge period should be less than or equal to X_2, the upper composition limit of the plateau region. This prohibits operation in the unfavorable region of the equilibrium isotherm, wherein the maximum pressure attained could be quite high.

b. The pressure at the end of the discharge period must be at least 1 atmosphere. The value of 1 atmosphere is chosen to ensure reasonable operation of the anode.

Equations (3) and (4) allow these limitations to be expressed quantitatively:

$$M \geq \frac{0.0187\ C}{X_2 - X(0)} \tag{5}$$

and

$$M \geq \frac{0.0187\ C}{t_D k(P_P - 1\ \text{atm.})} \tag{6}$$

Note that to obtain these expressions, the quantity RTMkt/V was taken to be >>1. For the cases considered herein this was true.

For calculations, the reservoir material was taken to be $LaNi_5$. Table III gives the pertinent quantities.

Calculations for $LaNi_5$ showed that use of the minimum amount of hydride led to the lowest weight system, and this minimum weight was used in all calculations.

Calculations were made for selected stack configurations from the gaseous storage cases. Fifty grams was arbitrarily added to the weight of the hydride cans to represent structural stiffening because of the thinness of the walls.

Hydride Anode Battery Design

There is evidence that hydride formation and decomposition may be carried out electrochemically in some metals and alloys, and such materials have been suggested for use as combined reservoir and anode in metal hydrogen systems. $LaNi_5$ is capable of such performance (ref. 2), and testing of a synergistic mixture of TiNi and Ti_2Ni has been reported (ref. 3).

Calculations were carried out for systems consisting of gaseous storage type stacks with the porous gas diffusion electrodes replaced by TiNi/Ti_2Ni anodes. Cans were of the hydride reservoir battery type.

The required anode thickness was calculated from

$$\delta_{\text{anode}} = \frac{C/n}{2\pi r^2 \gamma \rho_A^* (1 - \epsilon_A) e_A\ d_A}$$

where γ = ratio of active area to can cross-sectional area, ρ_A^* = theoretical material density, ϵ_A = anode porosity, e_A = anode specific capacity (amp-hr/g), and d_A the anodic depth of discharge. Table IV presents the values used, which were estimated from reference 3.

Calculations were carried out for selected stacks from the gaseous storage cases. Here too, 50 grams was added to can weights for structural stiffening.

Results and Discussion

Gaseous Storage Cells

Both nickel cathode and silver cathode stacks tended to exhibit a shallow minimum in stack weight as a function of number of subcells. Figure 4 shows the calculated stack weights for nickel cathodes and for the four different silver cathode stacks considered. The minimums result from the tradeoff between endplate weight and leads plus tierod weight.

Figure 4 also indicates that doubling cathode thickness (going from single to back-to-back cathodes) - and hence current density - substantially decreases stack weight. (Current densities corresponding to the cases of figure 4 are: nickel cathode - 37 ma/cm^2, silver cathodes, cases I and II - 170 ma/cm^2, cases III and IV - 85 ma/cm^2.) Finally, figure 4 indicates that even the heaviest silver cathode stack - that with single cathodes and IER's - is 40 to 50 percent lighter than the nickel cathode stack.

The maximum pressure developed within a cell utilizing gaseous storage occurs when the cell is fully charged and depends upon the stack ampere-hour capacity and the amount of gas filled volume within the can. Thus the smaller the can, the higher the maximum pressure and hence the thicker the can wall required. As the can volume increases the can weight goes through a minimum which represents a balance between wall thickness and size. Figure 5 shows the maximum pressure developed in the minimum weight and minimum volume cans for nickel cathode stacks.

Figures 6 and 7 give calculated gaseous storage cell weights and volumes, respectively. The effect of the design choice of initial pressure is shown for nickel cathode cells. While it does not have a large effect on cell weight, the choice of initial pressure does influence the volume of the minimum weight cell.

Figure 6 also shows the comparative cell weights associated with the lightest and heaviest of the four silver cathode stack options considered. Cell volume variations between the options are less pronounced and only the option yielding the largest volume is shown in figure 7.

Note that even the largest and heaviest silver cathode cells are smaller and lighter than their nickel cathode counterpart.

Hydride Containing Cells

With $LaNi_5$ as the reservoir material, equation (5) indicates that the minimum amount of material required to restrict operation to the plateau region of the equilibrium curve is approximately 165 grams for 50 ampere-hour systems. From equation (6), however, about 265 grams is required to keep the minimum pressure above 1 atmosphere. It is important to note that the limitation expressed by equation (6) is a direct function of the kinetic parameter - i.e., the rate behavior - of the hydride material. Thus in this case the minimum amount of hydride required is determined by rate considerations, while in the case of other hydride materials equilibrium characteristics - via equation (5) - may determine the minimum amount required.

The dynamics model indicates that there may be cases in which there is an optimum amount or weight of hydride, such that weight of reservoir plus can is minimized. The existence of such an optimum greater than the minimum depends on a number of factors which are unlikely to be encountered in practice. Also, maximum pressures in such systems are likely to approach those in low weight gaseous storage cells.

The maximum pressure reached during a 1-hour charge is 5 atmospheres in a cell containing 265 grams of $LaNi_5$. For a 10-hour charge the maximum pressure drops to 3.2 atmospheres. These maximum pressures are determined from equation (4) and can be seen to depend upon charge rate, amount of reservoir material present and hydride formation rate constant as well as plateau pressure.

Application of thin wall container design relations indicates that can walls need be 0.25 millimeters or less in thickness to contain these pressures, and such cans may weigh less than 20 grams. Rather than address the perhaps considerable problems of practical ultra-light weight can design, as mentioned above, 50 grams was arbitrarily added to the weight of hydride cans to obtain more conservative battery weights and gravimetric energy densities.

For comparative purposes cell weights and volumes were calculated for a 20-subcell nickel cathode stack and for 15-subcell silver cathode stacks of the four types considered. The comparative weights and volumes are given in Table V for hydride reservoir and hydride anode cells. It should be noted that hydride anode values may be inaccurate because of the lack of information regarding the hydrogen pressure above $TiNi/Ti_2Ni$ anodes.

Energy densities were calculated using total cell capacity and estimated mid-discharge voltage. The mid-discharge voltages used are given in Table VI. The voltage of hydride reservoir cells was taken to be 50 millivolts less than that associated with gaseous storage, because of the lowered hydrogen pressure. Hydride anode voltages were taken to be 150 millivolts lower, based on data in reference 3.

Gravimetric and volumetric energy densities are shown in figure 8.

Figure 8 indicates that silver cathode cells offer substantially higher gravimetric and volumetric energy densities than do nickel cathode cells. Among the silver cathode options, the use of IER's decreases gravimetric energy densities by about 25 percent and volumetric energy densities by 5 to 10 percent. The effect of doubling the cathode thickness is to increase gravimetric energy densities by 10 to 15 percent and volumetric energy densities by about 30 percent.

It appears that relatively high volumetric energy densities are attainable in gaseous storage cells without sacrificing too much gravimetric energy density if the attendant high pressures and large pressure changes can be tolerated. Hydride containing systems appear, however, to offer even higher volumetric energy densities and marginally higher gravimetric energy densities while radically diminishing the pressure related stresses imposed on the container in gaseous storage cells.

The present results indicate that the hydride reservoir approach offers somewhat higher energy densities than the hydride anode approach. Such a conclusion is, however, highly tentative because of the paucity of information on hydride anode behavior.

All the cases considered here appear to offer distinctly higher energy densities than do nickel-cadmium cells, which should fall in the 30 to 40 watt-hr/kg range for 100 percent depth of discharge. Corresponding volumetric energy densities for nickel-cadmium are in the vicinity of 50 to 70 watt-hr/liter, which is considerably lower than the volumetric energy densities attained by minimum volume gaseous storage and hydride-containing cells. Nickel-cadmium has however proven lifetimes of several thousand cycles at depths of discharge above 50 percent, which may be matched by nickel hydrogen, although such has not been demonstrated as yet. Silver-hydrogen lifetimes should prove to be at least several hundred cycles and should thus be comparable, if not better than silver-zinc at equivalent depths of discharge from the cycle life standpoint. Regarding energy density, silver-zinc cells can achieve 90 to 100 watt-hr/kg and 150 to 200 watt-hr/liter at 100 percent depth of discharge. Silver-hydrogen probably cannot exceed this gravimetrically, but minimum volume, gas storage and hydride-containing cells should be able to attain at least 50 percent higher volumetric energies.

References

1. Earl, M. W., and Dunlop, J. D., "Chemical Storage of Hydrogen in Ni/H_2 Cells," Preprint of Paper Presented at the Boston Meeting of the Electrochemical Society, Oct. 7-11, 1973.

2. Dunlop, J. D., Private communication.

3. Gutjahr, M. A., et al., "A New Type of Reversible Negative Electrode for Alkaline Storage Batteries Based on Metal Alloy Hydrides," Paper presented at the Power Sources Symposium, Brighton, England, 1972.

TABLE I. - QUANTITIES FOR GASEOUS STORAGE NICKEL-HYDROGEN CALCULATIONS

Fixed Parameters:

Ratio of sub-cell active area to cross-sectional area	0.93
Gas screen	
Thickness	0.05 cm
Porosity	0.5
Apparent density (weight/envelope volume)	1.0 g/cm^3
Porous gas diffusion anode	
Thickness	0.015 cm
Porosity	0.8
Apparent density	2.5 g/cm^3
Separator	
Thickness	0.025 cm
Porosity	0.8
Apparent density	0.4 g/cm^3
Electrolyte density	1.3 g/cm^3
Nickel cathode	
Thickness	0.152 cm (2×0.076 cm)
Porosity	0.7
Apparent density	3.25 g/cm^3
Specific capacity (complete discharge)	0.15 amp-hr/g
Gasketing	
Thickness	0.025×cell radius
Density	1.0 g/cm^3
Endplates	
Mean thickness	0.50 cm
Density	2.5 g/cm^3
Leads and tierod weight	2.5 g/subcell
Can material (Inconel)	
Density	8.45 g/cm^3
Yield stress	60 000 psi
Design safety factor	1.5
Feedthrough weight	30 g
Temperature	300 K

Independent Variables

Number of subcells in stack
Can length (gas storage volume) - see text
Precharge pressure

Dependent Variables

Stack radius
Stack thickness
Stack weight
Maximum pressure in container
Can wall thickness
Can weight
System weight
System volume
Current density

TABLE II. - QUANTITIES FOR GASEOUS STORAGE SILVER HYDROGEN CALCULATIONS

(Only those differing from Table I are given.)

Fixed Parameters

Silver cathodes	
Thickness	0.071 cm or 0.0142 cm
Porosity	0.5
Apparent density	5.28 g/cm^3
Specific capacity (complete discharge)	0.442 amp-hr/g
Inter-anode electrolyte reservoirs (see text)	
Pin field height	0.025 cm
Pin field coverage	0.5
Fullness factor	0.25
Material: sintered nickel	
Porosity	0.7
Apparent density	3.5 g/cm^3
Precharge pressure (independent variable in nickel-hydrogen calculations)	50 psia

TABLE III. - QUANTITIES FOR HYDRIDE RESERVOIR CALCULATIONS

(Only those differing from or not presented in Tables I and II are given.)

Fixed Parameters

Material: $LaNi_5$	
Plateau pressure	3 atm
Initial moles of H_2 as hydride per mole of $LaNi_5$ ($X(0)$)	0.50
Final moles of H_2 as hydride per mole of $LaNi_5$ (X_2)	3.0
Kinetic parameter (estimated from ref. 1)	0.765 (atm-hr)$^{-1}$
Apparent density	6.0 g/cm^3
Charge duration (t_c)	1 hour
Discharge duration (t_D)	1 hour

TABLE IV. - QUANTITIES FOR HYDRIDE ANODE CALCULATIONS

(Only those differing from or not presented in Tables I, II, and III are given.)

Fixed Parameters

Material: $TiNi/Ti_2Ni$	
Theoretical density	4.7 g/cm^3
Anode porosity	0.3
Effective specific capacity ($e_A \times d_A$)	0.25 amp-hr/g
Maximum pressure	10 atmospheres

TABLE V. - WEIGHTS AND VOLUMES OF HYDRIDE - CONTAINING CELLS (50 AMPERE HOUR)

	Stack or stack plus reservoir weight	Can weight	Cell weight	Cell volume
Nickel cathodes (20 cells)				
1. Hydride reservoir	990 g	98 g	1090 g	300 cm^3
2. Hydride anodes	890	130	1020	300
Silver cathodes (15 cells) Back-to-back cathodes, gas screens				
3. Hydride reservoir	490	85	580	110
4. Hydride anodes	430	93	520	110
Silver cathodes (15 cells) Back-to-back cathodes, IER				
5. Hydride reservoir	630	85	720	140
6. Hydride anodes	570	95	670	160
Silver cathodes (15 cells) Single cathodes, gas screens				
7. Hydride reservoir	560	89	650	140
8. Hydride anodes	490	100	590	150
Silver cathodes (15 cells) Single cathodes, IERS				
9. Hydride reservoir	680	89	770	160
10. Hydride anodes	610	110	720	180

TABLE VI. - MID-DISCHARGE VOLTAGES

Nickel cathodes; gaseous storage	1.26 Volts
Nickel cathodes; hydride reservoir	1.21
Nickel cathodes; hydride anodes	1.11
Silver cathodes; gaseous storage	1.10
Silver cathodes; hydride reservoir	1.05
Silver cathodes; hydride anodes	.95

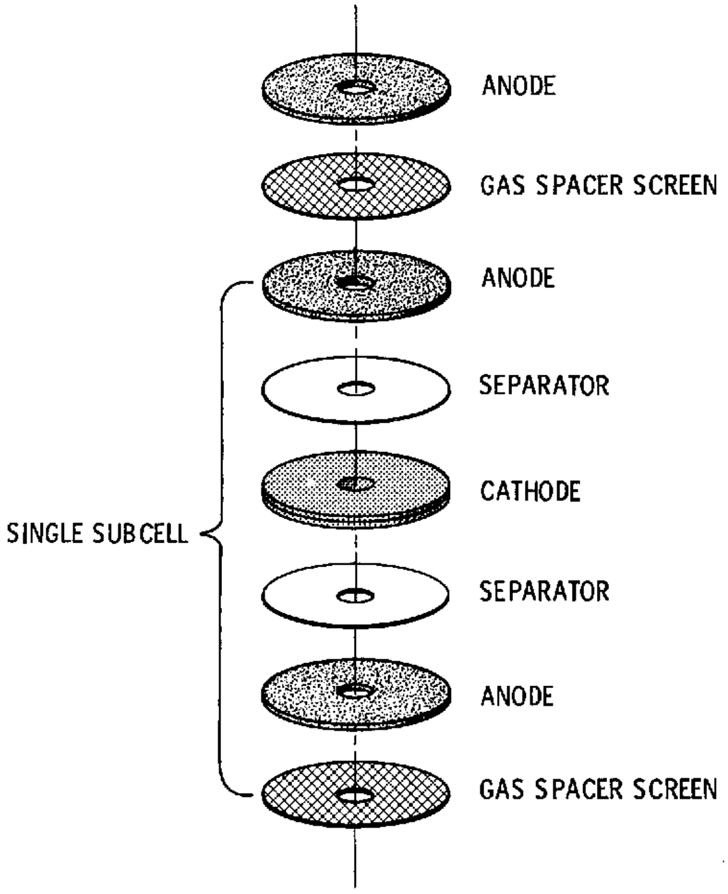


Figure 1. - Gaseous storage nickel hydrogen stacking sequence.

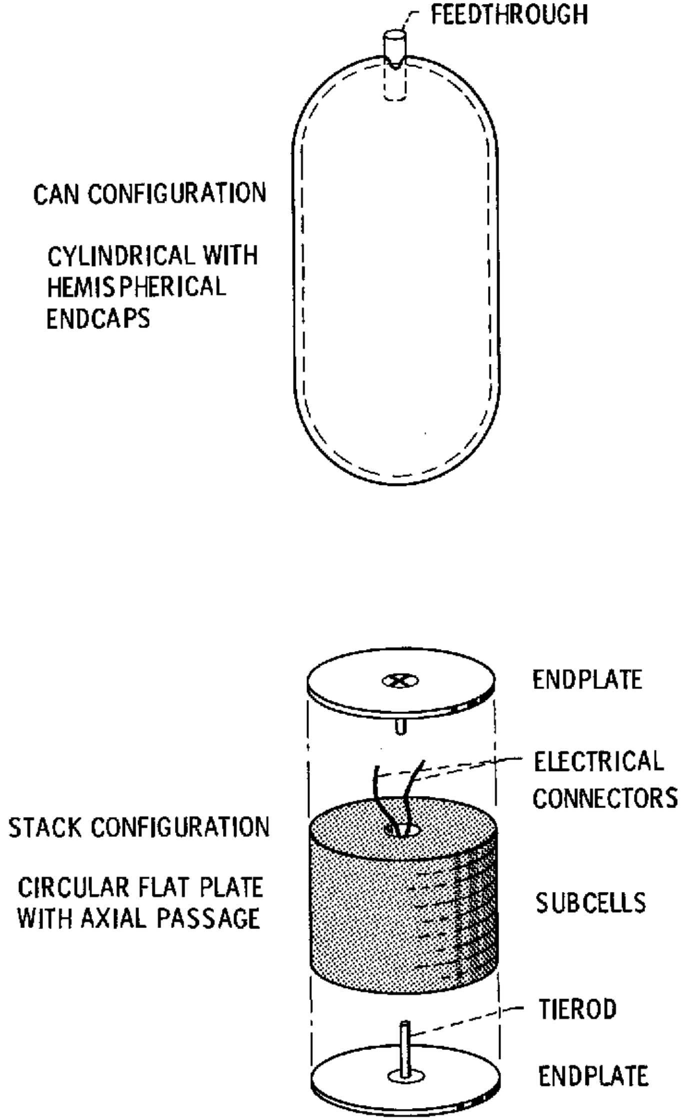


Figure 2. - Gaseous storage nickel hydrogen can and stack configurations.

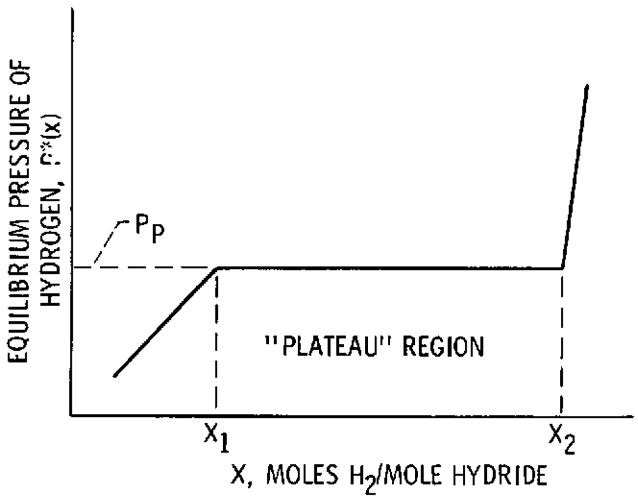


Figure 3. - Idealized hydride isotherm.

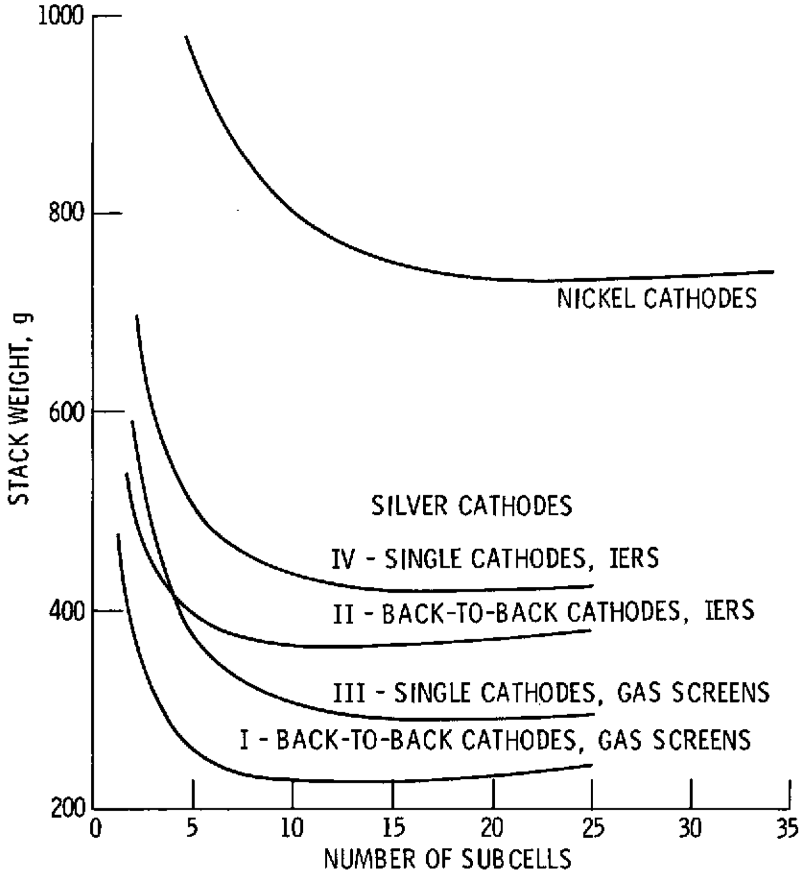


Figure 4. - Stack weights as function of number of subcells. Fifty ampere-hour capacity; porous gas diffusion anodes.

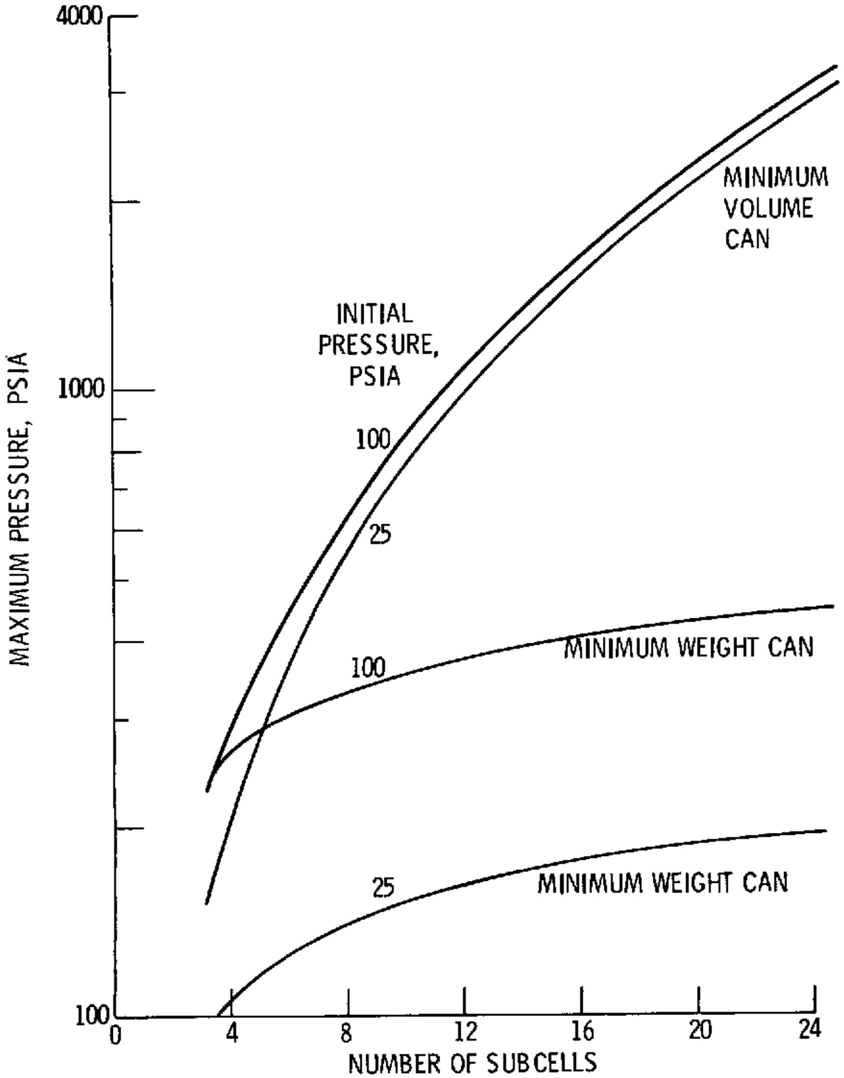


Figure 5. - Maximum pressure as function of number of subcells. Gaseous storage cans; nickel cathode stack.

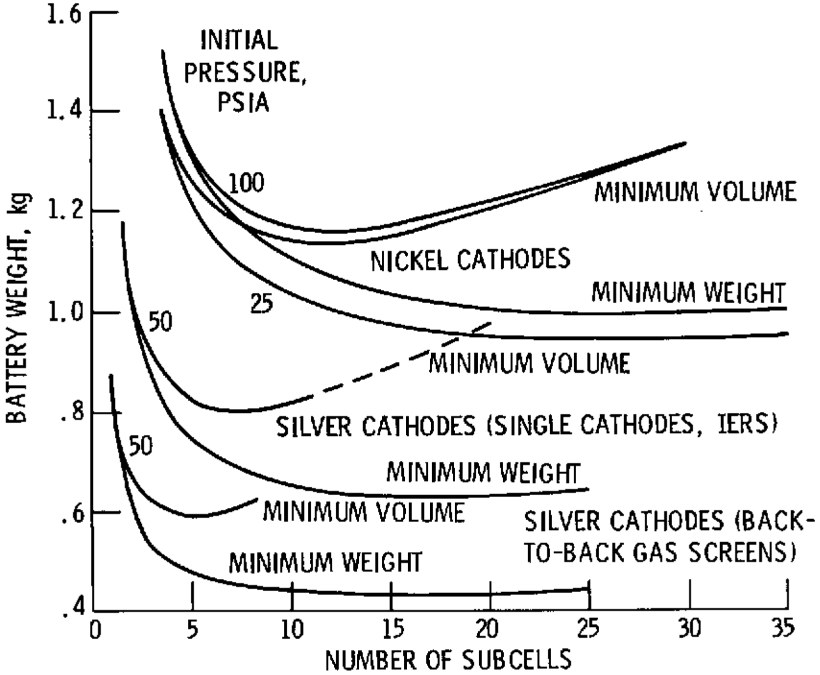


Figure 6. - Battery weight as function of number of subcells. Gaseous storage. (Note: Dashed lines indicate that the thin wall container design relations are of doubtful validity.)

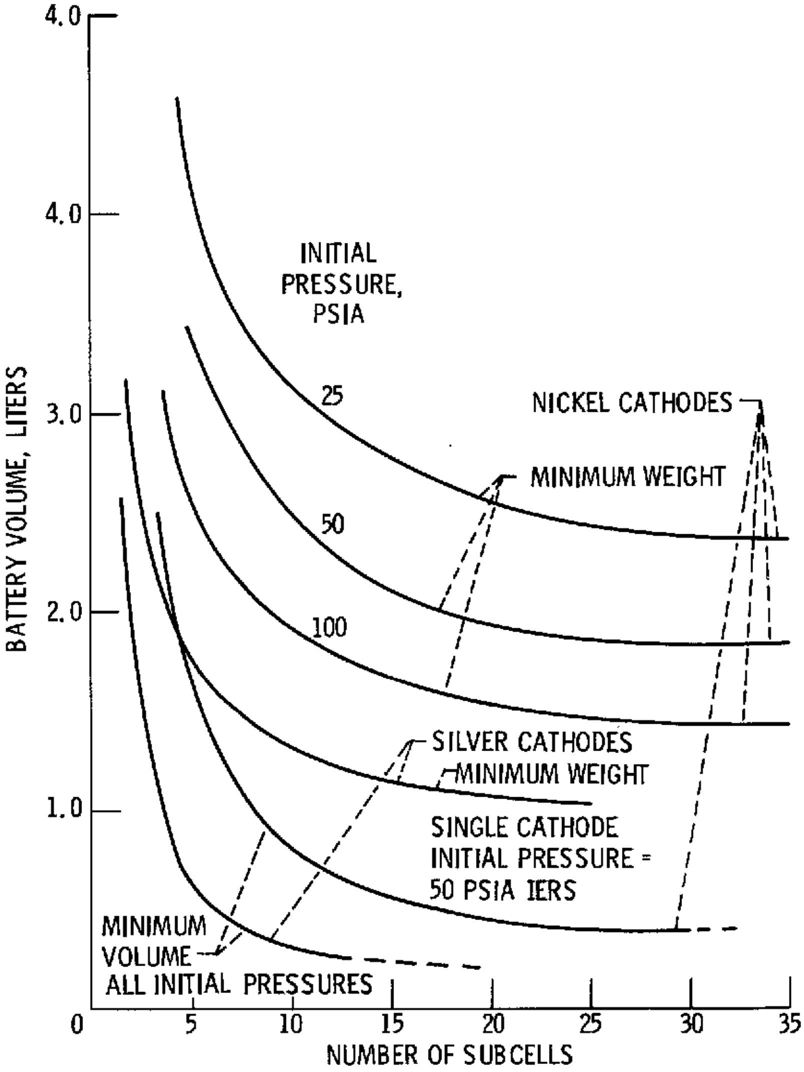
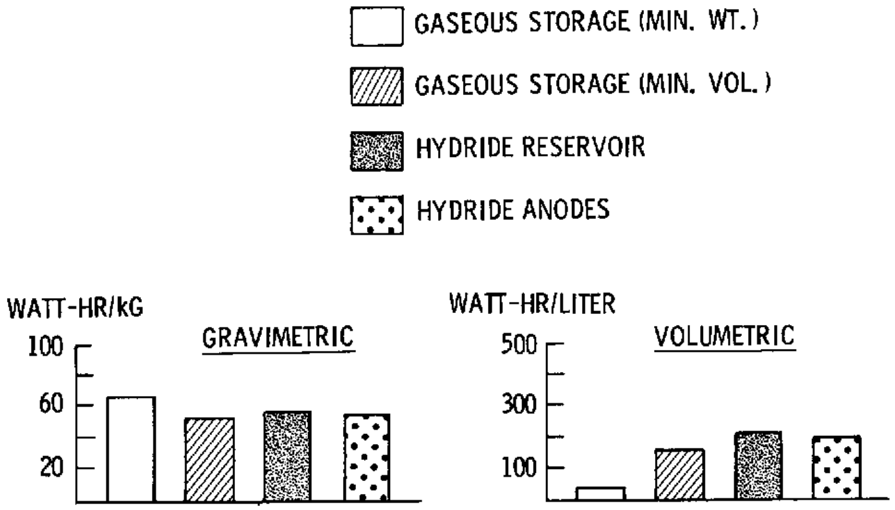
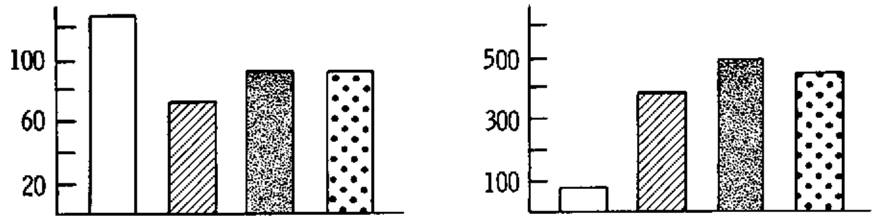


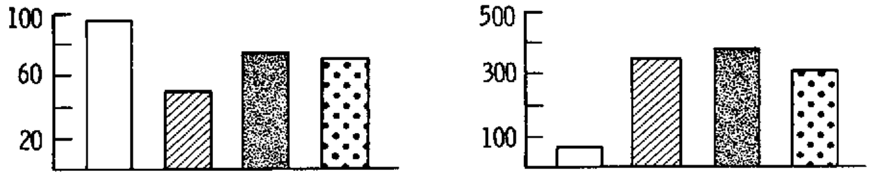
Figure 7. - Battery volume as function of number of subcells. Gaseous storage.



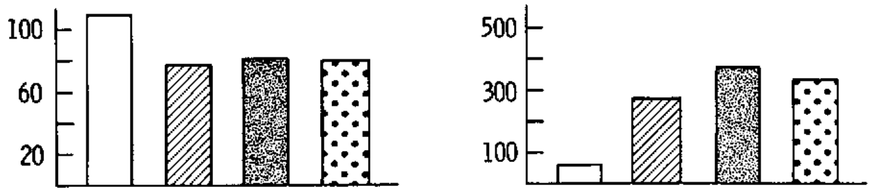
NICKEL CATHODES (20 SUBCELLS)



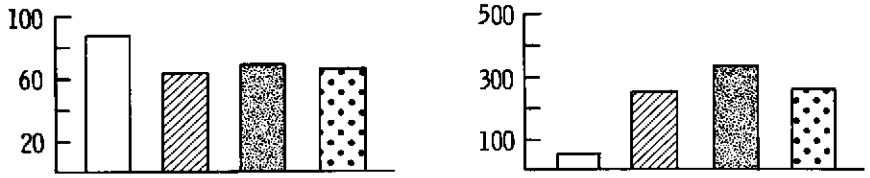
SILVER CATHODES (15 SUBCELLS) BACK TO BACK; GAS SCREENS



SILVER CATHODES (15 SUBCELLS) BACK TO BACK; IERS



SILVER CATHODES (15 SUBCELLS) SINGLE CATHODES, GAS SCREENS



SILVER CATHODES (15 SUBCELLS) SINGLE CATHODES, IERS

Figure 8. - Fifty ampere-hour metal-hydrogen cell energy densities.

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