

A NEW CONCEPT FOR HIGH-CYCLE-LIFE LEO: RECHARGEABLE MnO_2 -HYDROGEN BATTERIES

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Summary

The nickel-hydrogen secondary battery system, developed in the early 1970s, has become the system of choice for geostationary earth orbit (GEO) application. However, for low earth orbit (LEO) satellites with long expected lifetimes the nickel positive limits performance. This requires derating of the cell to achieve very long cycle life. A new system, rechargeable MnO_2 -hydrogen, which does not require derating, is described here. For LEO applications, it promises to have longer cycle life, higher rate capability, a higher effective energy density, and much lower self-discharge behavior than those of the nickel-hydrogen system.

Introduction

Space power systems designed for continuous high-power-output applications have most commonly been based on the use of photovoltaic panels. Since, in all orbits, satellites are subjected to a greater or lesser number of eclipses, a reliable means of energy storage and power load-leveling is required using reliable, maintenance-free secondary batteries. In the early 1970s, nickel-cadmium was the only proven long-lived secondary battery for use in space. Most of its long-term applications were in GEO communications satellites, for which there are two 45-day eclipse periods per year and one eclipse per eclipse-day in typical orbits. The eclipses are of variable duration, and reach a maximum of 1.2 h at the middle of the eclipse period. Over a ten-year satellite lifetime, a total of about 900 cycles are therefore required, varying from a maximum of medium discharge (60% depth of discharge, DOD) at the $C/2$ rate for 1.2 h, to shallow discharge, 60% DOD being a precautionary choice for long lifetime and reliable operation. Typical aerospace Ni-Cd cells can easily exceed 2000 cycles under these cycling conditions, but in a battery their energy density is little better than 20 W h kg^{-1} . In view of the importance of battery weight in determining overall power system weight, hence, incremental satellite structural

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weight, new battery concepts offering higher specific energy were explored. As an illustration of the battery contribution to power system weight, state-of-the-art deployable photovoltaic (PV) panels have a specific power of 55 W kg^{-1} , whereas the Ni-Cd battery under the above discharge conditions has a specific power of 16.7 W kg^{-1} . Thus, 18.2 kg of PV array is required to produce a continuous 1 kW output, with an additional 1.2 kg (three-axis stabilization) to charge an 80% efficient battery over 22.8 h per eclipse-day, discharging in 1.2 h with a power output of 1 kW. Based on 16.7 W kg^{-1} , such a battery would weigh 60 kg, thus demonstrating the driving force for reducing battery weight.

High-energy-density satellite batteries

The first attempt to reduce battery weight was the development of a regenerative fuel cell/electrolyzer (RFC) in the 1960s [1]. This consisted of a thin, lightweight pressure vessel containing pure noble metal negative and positive electrodes of fuel cell type, with a separator containing KOH electrolyte. A flexible, sealed divider cut the pressure vessel into two volumes in the ratio 2:1 to store hydrogen produced at the negative and oxygen at the positive. The gases were recombined at the same electrodes. The system should be capable of many deep-discharge cycles, with indefinite cycle-life at the hydrogen electrode, and long life at the oxygen electrode provided that suitable electrocatalysts (*e.g.*, gold-iridium) are used. A calculation shows that 54 W h kg^{-1} is obtainable [2], assuming an Inconel 718 pressure vessel with a safety factor of 4. This is over twice the value for Ni-Cd. However, the state-of-the-art electrocatalyst technology could not offer a round-trip efficiency greater than about 50% due to oxygen electrode polarization. More importantly, the storage system was subject to cross-leaks, which limited reliability, lifetime, management of the excess water produced on discharge and consumed on charge, and proved to be a problem. In spite of these drawbacks, an updated version of this system using more recent technology may still have advantages for certain applications [2].

To avoid cross-leaks and electrolyte management problems, attention was transferred to metal-oxygen battery concepts. These can, in principle, show high energy density (for example, the zinc-oxygen couple has a theoretical energy density of 600 W h kg^{-1}), and the open volume of the pressure vessel (about 60% of the weight of the RFC) is small, since only oxygen storage is required. In consequence, zinc-oxygen systems (which do not have a water-management problem since the discharge product is simply zinc oxide) were estimated to have practical energy densities of the order of 90 W h kg^{-1} [3]. However, like all alkaline-zinc systems in stationary electrolyte, the negative showed dendrite formation and shape-change, resulting in limited cycle-life. The zinc electrode can also react explosively with excess oxygen on overcharge, which is accompanied by drying out.

Finally, while the coulombic efficiency of the zinc-oxygen system is good, the oxygen electrode charge-discharge characteristics limit voltage efficiency to 60%. Since the corresponding cadmium system [3] has only the advantage of cycle life over zinc-oxygen, with a considerably poorer energy density, attention focussed on metal-oxide/hydrogen systems, specifically nickel-hydrogen, which combined the best electrodes of the Ni-Cd and RFC.

The nickel-hydrogen system

The Ni-H₂ battery combined the two electrodes from the Ni-Cd battery and the RFC with the best electrochemical characteristics. Both operate close to reversibility, and give high coulombic efficiency. The battery was first described in the patent literature [4], and was developed from 1970 onwards, primarily at Comsat Laboratories [5]. No attempt was made to use specially-developed components for the battery. Compared with zinc-oxygen, it was immediately obvious that the nickel-hydrogen system would be conservative from the viewpoint of energy density. Aerospace Ni-H₂ positives of conventional construction have a typical capacity of 0.11 A h g⁻¹, which is perhaps only 20% of that of a zinc negative, and hydrogen negative systems require twice the container volume and weight of those using oxygen positives. While a lightweight design, with a minimum container safety factor, might achieve 55 W h kg⁻¹, a more practical figure is 45 W h kg⁻¹ on the single-cell level [5].

The Ni-H₂ system has no problems of electrolyte management, since the overall cell reaction:



does not involve formation or consumption of free water. This represents an advantage over both the RFC and the Ni-Cd system. The hydrogen electrode operates under benign conditions, at high hydrogen pressures (up to several hundred psi) and with maximum current densities of about 40 mA cm⁻² at the *C* rate. There is no evidence of change of hydrogen electrode performance with time under normal operating conditions. While the nickel electrode has an enviable record of longevity, it is still the life-limiting element in the battery. Since the nickel electrode operates in a starved electrolyte environment, any electrolyte loss from the separator can cause cell failure. With chemically-impregnated aerospace electrodes, failure occurred at about 2500 cycles under GEO cycling conditions with 50% over-charge per cycle. Corrosion of the nickel sinter, with consequent consumption of water, was identified as the cause of failure [6]. Improved lifetimes (to about 5000 cycles) were observed with under-impregnated electrodes, and with electrochemically impregnated electrodes [7], which have a more uniform distribution of active nickel hydroxide in the sinter structure [6].

On cycling, swelling of the nickel electrodes occurs, resulting from volume changes in the active material. Corrosion of the sinter, in effect,

produces more active material, but the internal stresses created cause progressive breakdown of the sinter by the rupture of the "necks" between individual nickel particles. Since the electronic pathways through the sinter are thereby compromised, capacity slowly falls after going through a maximum early in life. Eventually, breakdown is total, and the cell ceases to function, even if electrolyte losses are made up. The situation is improved by using lower active material loadings, and by operating the electrodes at lower depths of discharge, keeping overcharge to a minimum. This demonstrates the effect of rate on cycle life.

For LEO applications, charge/discharge rates are not only much higher than those for GEO, but a far larger number of cycles is required. In an equatorial orbit, sunlight is 0.9 h, and the eclipse period is 0.6 h, with one charge-discharge cycle per orbit, or 5840 cycles per year. Consequently, for a guarantee of a ten-year lifetime, over 100 000 cycles would have to be reliably demonstrated in laboratory testing. Thus far, 8000-12 000 cycles can be routinely demonstrated with low-loading, electrochemically impregnated electrodes. One aspect of recent work has been the effect of initial electrolyte concentration on cycle-life. It has been shown that life is at a maximum at a starting concentration of 26% KOH, when about 30 000 LEO cycles can be achieved with derated electrodes [8]. This seems to suggest that two different processes control electrode lifetime, one perhaps being charge acceptance of the nickel positive, which is favored at higher electrolyte concentrations, and the limiting effects of sinter corrosion, which also become more marked at high concentrations. However, in spite of this work, it would appear that the nickel electrode, at least in its present form, is marginal for long-term LEO use.

The rechargeable MnO_2 positive

Electrolytic manganese dioxide has only a limited charging ability (about 50% of the first electron) [9]. However, in recent years a highly rechargeable form of MnO_2 has been demonstrated in which both electrons can be reversibly charged and discharged. This consists of a material doped with bismuth (1 - 5 at.%), with birnessite structure [10 - 12]. It can be subjected to many thousands of rapid cycles (at the 12 C rate in thin electrodes) and still shows no noticeable degradation in performance (Fig. 1). It is quite indifferent to overcharge (no formation of soluble species) and to overdischarge. Unlike electrolytic MnO_2 , both electrons discharge in the same potential range, giving a very flat discharge plateau and a more useful capacity to the voltage cut-off point, as Fig. 2 shows for a cell with a zinc negative. In a benign environment (*i.e.*, in the absence of certain impurities in the electrolyte) 85% of the two-electron capacity can be recovered over an indefinite number of cycles. Like Ni-H_2 , $\text{MnO}_2\text{-H}_2$ has no water management problems, since the overall cell reaction is $\text{MnO}_2 + \text{H}_2 \Rightarrow \text{Mn(OH)}_2$. Finally, overall efficiency is estimated to be 78% (similar to Ni-H_2), and heat dissipation has similar characteristics to those of Ni-H_2 .

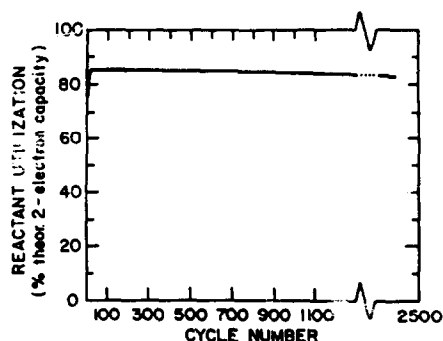


Fig. 1. Reactant utilization *vs.* cycle number for a modified MnO_2 electrode cycled at 6 C in 9 M KOH at room temperature.

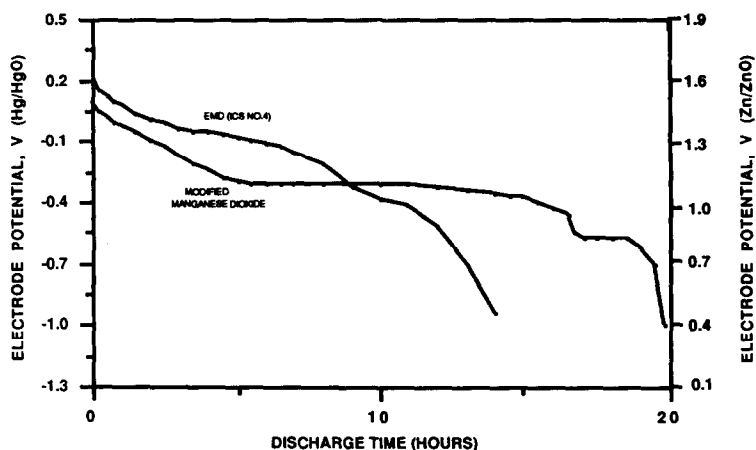


Fig. 2. First discharge curve for electrolytic MnO_2 and modified MnO_2 obtained in 9 M KOH at room temperature with a discharge current of $44 \text{ mA g}^{-1} \text{ Mn}$. Cathode mix: 85 wt.% manganese dioxide, 10 wt.% acetylene black and 5 wt.% binder.

At first sight, the proposal of using the modified MnO_2 positive combined with a hydrogen electrode does not make much sense, since the couple has a comparatively low voltage compared with that of nickel-hydrogen (average plateau potential at LEO rates is approximately 0.7 V *versus* hydrogen at an average pressure of 24 atm). However, the low potential has certain operational advantages that are conducive to long life and low corrosion rates. In addition, since the modified MnO_2 positives can be operated at a nominal 85% of their two-electron capacity in long-term cycling, even at high rates, the positives are much lighter and have smaller volumes than nickel electrodes. Finally, microcalorimeter measurements (Fig. 3) have established that the rate of the self-discharge reaction between MnO_2 and compressed hydrogen is much less than that for NiOOH . The mild corrosion environment allows the use of graphite powder additive as an electronic conductor in Teflon-bonded electrodes. With a material doped with

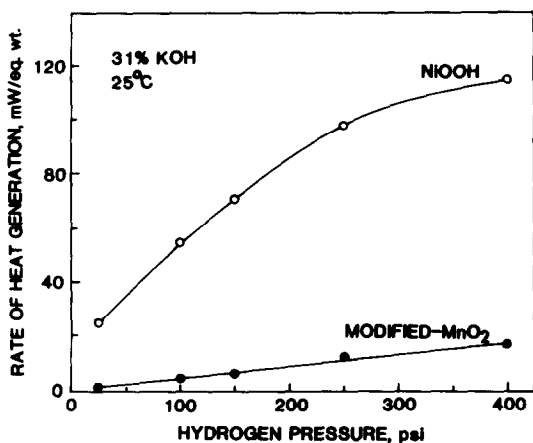


Fig. 3. Heat generation rates as a function of hydrogen pressure from the reactions between hydrogen and NiOOH and bismuth-modified MnO₂. 0.1 g oxide samples in 1.0 ml of 31 wt.% KOH were used.

2 at.% bismuth, containing 15 wt.% graphite and 7 wt.% Teflon binder, the specific coulombic yield of the positive mix is 0.43 A h g⁻¹ to 85% DOD. Applied to a screen similar to those used for hydrogen electrodes, this value is reduced to 0.249 A h g⁻¹.

Comparison between modified MnO₂-H₂ and Ni-H₂ for LEO use

Table 1 shows a breakdown of component weights in a Ni-H₂ cell with a nominal capacity of 38.5 A h (to 1.0 V at 23 °C). The volume of the Inconel 718 container (with safety factor of 4) has been arranged to contain 38.5 A h of hydrogen between 41 and 7 atm. To ensure very long cycle life under LEO conditions, the positive electrodes in such a system must be derated, typically to 40% of capacity. This requires a larger stack weight and volume, since the number of positives, negatives, separators, and gas streams, together with the total electrolyte volume, must be increased by 2.5. In consequence, the container weight and volume must be correspondingly increased. Overall, the LEO Ni-H₂ cell has an effective specific energy of 22.2 W h kg⁻¹ (33.1 W h l⁻¹), whereas the baseline Ni-H₂ has values of 44.9 W h kg⁻¹ and 51 W h l⁻¹.

The final column contains the corresponding breakdown for LEO MnO₂-H₂. It can be seen that the smaller weight and volume of the positives result in a lighter and more compact cell than baseline Ni-H₂, although its specific energy is degraded by its lower operating voltage. However, in the LEO application it offers a specific energy of 32.6 W h kg⁻¹, almost 50% higher than the purpose-designed Ni-H₂ cell with derated electrodes,

TABLE 1
Cell weight breakdown (g)

Component	Nominal Ni-H ₂	LEO Ni-H ₂	LEO MnO ₂ -H ₂
Positives	348.6	870.5	154.4
Hydrogen electrodes	72.0	180.0	72.0
Separators	35.1	87.8	35.1
Gas screens	8.0	20.0	8.0
Electrolyte	159.0	397.5	159.0
Stack total	622.7	1555.8	428.5
Center rod and insulator	14.3	35.8	14.3
Busbars and tabs	41.4	41.4	41.4
Endplates	34.0	34.0	34.0
Nuts, washers	4.6	4.6	4.6
Terminal conductors	79.0	79.0	79.0
Internal hardware	173.3	194.8	173.3
Pressure shell	179.0	275.4	170.5
Weld ring	35.0	35.0	35.0
Compression seals	18.4	18.4	18.4
Container	232.4	328.8	223.9
Total cell weight	1028.4	2079.4	825.7
Total cell volume (ml)	836.0	1286.0	805.0
Specific energy (W h kg ⁻¹)	44.9	22.2	32.6
Specific energy (W h l ⁻¹)	51.0	33.1	33.5

intended for the same application. On a W h l⁻¹ basis, both systems have the same practical energy density.

Conclusions

The proposed modified MnO₂-H₂ cell operating at 0.7 V (nominal), with electrodes operating at 85% of two-electron capacity, has the same volume energy density as Ni-H₂ operating with positives derated to 40% of capacity to achieve 25 000 or more LEO cycles. Its energy density on a weight basis is 50% greater (32.6 W h kg⁻¹). The relatively low operating potential of the MnO₂ positive means that it operates in a mild environment from the viewpoint of corrosion, ensuring long life with graphite as an electronically conducting element in the structure. Microcalorimeter studies have demonstrated a low self-discharge rate for the positive. In view of the above, and taking into account the difficulty of making nickel positives that can reliably offer 50 000 or more cycles, the secondary MnO₂-H₂ system deserves serious consideration for LEO use.

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