

Common vessel monoblock design for sealed nickel-cadmium batteries

Boris Tsenter, Menahem Anderman

Acme Electric Corporation, Aerospace Division, Tempe, AZ 85 282, USA

Received 1 March 1995; accepted 14 June 1995

Abstract

A new common vessel monoblock (CVM) design has been developed for large sealed Ni-Cd batteries. The battery is managed as one sealed monoblock unit rather than a number of individual Ni-Cd cells. The CVM combines flooded battery cells and a Cd-H₂ cell (regulator) for consuming hydrogen, oxygen or both. The cells share a common gas space and the regulator is in gaseous communication with battery cells and maintained under constant voltage. A 'smart-charge' monitors the battery pressure, battery current, and regulator current and temperature. This battery system automatically supports the individual cell's water balance by means of water vapor transport in the common gas space. On-charge heat is produced only in the regulator and not at all in the battery cells. This condition coupled with the flooded electrolyte individual cell design and sealed battery concept, alleviates many problems associated with large sealed cell battery designs. The maintenance-free, fully automated control and fast charge capability makes the CVM battery an attractive solution for industrial and electric vehicle (EV) applications. In this paper, the design and operating principles of the CVM and test data on 100 Ah 12 V module will be discussed.

Keywords: Common vessel monoblock; Nickel; Cadmium; Batteries

1. Introduction

The standard sealed cell design does not easily lend itself to high voltage battery applications. Specific concerns are associated with thermal imbalance that causes capacity imbalance and limited robustness to overcharge or cell reversal. The purpose of this paper is to describe the new common vessel monoblock (CVM) battery design that employs vented cell construction in a common vessel sealed battery [1,2]. This battery design offers the robustness of the vented cell in a maintenance-free, sealed battery managed on the battery level.

2. Description of the CVM battery design

The CVM battery design is shown in Fig. 1.

The flooded electrolyte battery cells are installed in a sealed container and connected electrically in series, sharing a common gas space. The electrochemical, metal-hydrogen pressure regulator is located in the same sealed container and also shares the same common gas space as the flooded cells. There is a minimum of one independent electrical terminal. The regulator is a metal-hydrogen cell (Me|KOH|H₂) comprised of metal (e.g. cadmium) and hydrogen reversible elec-

trodes with starved electrolyte, described in Ref. [3]. The concept to utilize a special device outside the battery's cells was originally conceived at the St. Petersburg Battery Institute, Russian Federation. However, this was a passive cadmium-hydrogen regulator without an external power supply. This system was incapable of consuming hydrogen at an acceptable rate as the overvoltage for this process was less than the open-circuit voltage (OCV) of the cadmium-hydrogen couple, which equals 30 mV.

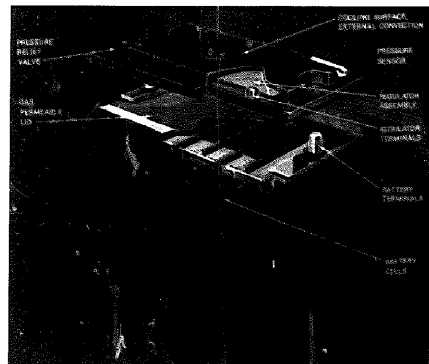


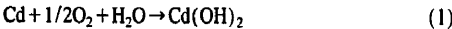
Fig. 1. Schematic diagram of the monoblock design.

According to our design, the active regulator is maintained at 0.05–0.60 V above the OCV of the regulator cell. At lower voltages the rate of hydrogen consumption is too low and at higher voltages the rate of oxygen consumption is too low. Fig. 2 depicts the partial polarization curves for hydrogen and oxygen consumption. Regardless of gas being consumed, the gas electrode has positive polarity and the metal electrode of the regulator has negative polarity. The Cd–H₂ regulator has OCV equal to 0.030 V and should be maintained at 0.08 V < V_r < 0.63 V. A 0.40 V value for the regulator's voltage was found to be optimal for the 12 V 100 Ah CVM Ni–Cd prototype battery.

The regulator provides the functions of oxygen consumption, hydrogen consumption and heat dissipation. This paper describes the regulator's operation at initial vacuum. The battery employs a pressure sensor and a temperature probe. Gas, water, heat and charge transfer occurs between the battery cells and the regulator in the CVM design. However, there is also a version of regulator's operating with hydrogen precharge, which can be used for metal–hydride chemistry.

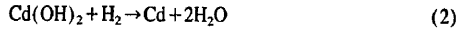
2.1. Gas transfer

Oxygen evolved during overcharge is reduced on the hydrogen electrode and cadmium is oxidized on the counter electrode. The summary reaction occurring in the regulator during oxygen consumption is:



This operates as a galvanic Cd–O₂ couple, producing energy equal to the product of the regulator's voltage and current, as per the summary Eq. (1) oxygen is consumed at the voltage of the regulator cell. The regulator voltage 0.40 V provides sufficient overvoltage for the process of oxygen reduction, according to Fig. 2.

The CVM design offers a unique opportunity to consume hydrogen as well. Hydrogen produced at the cadmium electrode of the battery cells during charge is consumed at the regulator per the following summary reaction:



Per Eq. (2), hydrogen is consumed at the same voltage as the regulator's voltage 0.40 V. An electrolytic Cd–H₂ couple consumes the energy from the charger equal to the product of the regulator's voltage and current. The hydrogen electrode's polarity is positive and the cadmium electrode polarity is negative, as in the case of oxygen consumption. This means that it is possible to consume either hydrogen or oxygen while maintaining the regulator's voltage at 0.08 V < V_r < 0.63 V, with the gas electrode remains positive and the cadmium electrode remains negative. The net product of both Eqs. (1) and (2) is water and the cadmium electrode works as a buffer for the compensation of non-stoichiometric hydrogen–oxygen mixture. The stoichiometric amount of oxygen–hydrogen mixture can be consumed chemically at the gas electrode as per reaction:



During battery charge, the balance equation describing the pressure variation in the CVM design is:

$$(dP/dt)/a_0 = 1/2I^H + 1/4I^O - 1/2I_H - 1/4I'_O - 1/4I'_{H_2O} - 3/4I_{H_2O} \tag{4}$$

where *P* is total pressure during time, *t*, *a*₀ = *RT*/*FV* the vessel constant, *V* the free gas volume, *I*^H and *I*^O the currents of hydrogen and oxygen production respectively, *I*_H and *I*_O are the currents of hydrogen and oxygen electrochemical consumption at the regulator, *I*'_O and *I*'_{H₂O} are the rates of oxygen consumption at the cadmium electrode and chemical consumption of the hydrogen–oxygen mixture in the regulator, respectively.

If only oxygen is produced, then: *I*^H = *I*_H = *I*'_{H₂O} = 0 and Eq. (4) is rewritten as:

$$(dP/dt)/a_0 = 1/4I^O - 1/4I'_O - 1/4I'_{H_2O} - 3/4I_{H_2O} \tag{5}$$

2.2. Water transfer

The water balance in the CVM battery is self-regulated. Oxygen produced during the charge cycle combines with hydrogen in the regulator to form water, thus diluting the regulator electrolyte and concentrating the electrolyte in the battery cells. Since the vapor pressure of water is inversely proportional to KOH concentration, water evaporates from the more dilute solution and condenses in a more concentrated solution. Some circumstances accelerate the diffusion rate. Although the rate of water transfer is greater during the oxygen recombination process, the duration is limited to the inefficient amount of charge and overcharge. The CVM battery operates with very low total pressure when idle and water is transferred in the process of vacuum evaporation. Evaporation and condensation occur at all times.

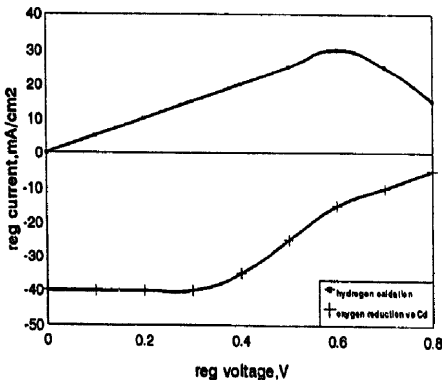


Fig. 2. Volt-ampere characteristics of hydrogen and oxygen consumption.

2.3. Heat transfer

The regulator's heat dissipation function is provided as follows: oxygen, produced at the positive electrode of the battery on-charge, is consumed at the hydrogen electrode of the regulator.

A good approximation of the power dissipated at charge in the CVM is written as:

$$W = (V - E^{T0})nI + (E^{T1} - V_r)I_0 + E^{T1}I'_0 + (V_r - E^{T2})I_H + E^{T3}I_{H_2O} \quad (6)$$

where V and I are charge voltage per cell and current for battery of n cells, respectively, and V_r is regulator's voltage; E^{T0} , E^{T1} , E^{T2} , E^{T3} are thermoneutral potentials of the Ni-Cd (1.45 V), Cd-O₂ (1.43 V); Cd-H₂ (0.073 V) and H₂-O₂ (1.48 V) cells, respectively [4,5].

The first term of Eq. (1) relates to heat dissipation in the battery cells and an additional four terms relate to the heat dissipation in the regulator.

The charge voltage per cell of the Ni-Cd system varies between 1.40-1.70 V so that the first term (heat dissipation in the cells) of Eq. (4) is only a small fraction of the total heat produced. Therefore, heat generation depends mostly on the reactions occurring in the regulator and the deteriorative effects of overheating the battery cells are minimized.

2.4. Charge transfer

It is necessary to emphasize that the CVM battery is a self-balanced design. The regulator ratio of metallic cadmium to cadmium hydroxide will oscillate around a definite value. With oxygen production during charge, metallic cadmium accumulates on the negative electrode of the battery cell and cadmium hydroxide accumulates in the regulator. Upon discharge, the battery cells will still retain some metallic cadmium.

On the following cycle, more hydrogen is produced from the battery cells and the excess transfers cadmium hydroxide in the regulator to metallic cadmium. If more hydrogen is produced, the nickel oxide electrode capacity increases as compared to the cadmium electrode and produces more oxygen on the following cycle. The regulator can be regarded as an independent device that supports the intermediate balance of the cell's electrodes.

3. Experimental

A 10 cell 100 Ah prototype Ni-Cd CVM design was constructed to verify the monoblock concept for a large scale battery. Each cell contains 11 nickel oxide fiber electrodes and 11 cadmium fiber electrodes. The ratio between available capacity of cadmium and nickel electrodes is 1.05. The battery cells operate in the flooded mode with electrolyte concentration of 8 N KOH + 0.8 N LiOH. Each regulator cell

contains six pairs of cadmium electrodes and seven pairs of hydrogen electrodes in a back-to-back configuration separated by a metallic gas diffusion screen. The hydrogen electrodes in the regulator are of the same design used in nickel-hydrogen technology. One layer of polypropylene separator is used. The available cadmium capacity of one regulator is 60 Ah and the electrolyte is 9 N KOH. The experimental CVM battery contains ten series connected Ni-Cd cells. All cells share a common gas space with two regulator cells. The battery is equipped with a pressure sensor and a thermal sensor.

Full discharge capacity of the battery is 100 Ah after a 120 Ah charge at 50 A in the vented mode. An in-house produced 'smart-charger' is used to regulate the battery. This smart-charger is capable of providing 1400 W of output power with a maximum of 18.5 V terminal voltage at 75 A. The regulator is capable of generating a maximum of 50 A at 0.6 V in charge/discharge modes. The battery charge voltage and current, the regulator charge/discharge voltage and current, the battery and regulator state-of-charge, the battery and regulator temperature, and battery pressure are all monitored. The battery operates with an initial pressure equal to zero. Regulator voltage is maintained at 0.40 V in such a manner that the hydrogen electrode is positive in relation to the cadmium electrode at all times. Battery current is regulated stepwise in response to battery pressure. The charge is terminated if the battery pressure or regulator temperature exceeds a pre-determined level.

4. Results and discussion

Testing of the prototype 10 cell 100 Ah CVM battery demonstrates the feasibility of this design. Fig. 3 shows the battery current, regulator current and pressure versus state-of-charge. Initial charge current equals 50 A ($C/2$). In the

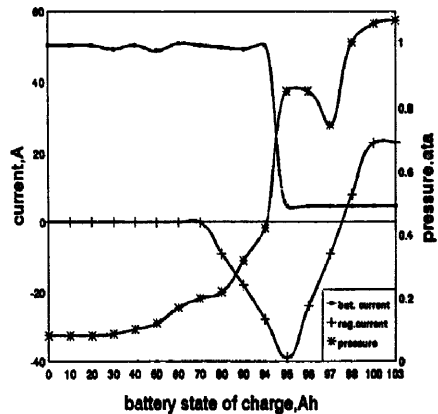


Fig. 3. Charging characteristics at 25 °C; pressure, battery current, and regulator current vs. state-of-charge. Initial charge current = 50 A, and discharge capacity = 97 Ah.

beginning, the regulator current has a negative direction. This means that oxygen consumption occurs according to Eq. (1). At 96% state-of-charge, pressure triggers a decrease in charge current. The drop in regulator current direction suggests that hydrogen evolution takes place at this point. The pressure's profile depends upon a balance of the rate of gas generated in the battery cells and consumption in the regulator. According to the data in Fig. 3, the rate of electrochemical oxygen consumption (regulator current) is 39 A after delivering 96 Ah of charge capacity to the battery. The rate of oxygen consumption at the cadmium electrode was calculated from the rate of pressure drop after termination of charge. This was found to be 32 A at 0.95 atm oxygen pressure. Total oxygen consumption is 71 A (7.1 A/cell) and is equal to the rate of oxygen production because dP/dt is zero at this point (Eq. (5)).

The nickel oxide electrode charge efficiency equals 86% at the 96% state-of-charge. This high rate of efficiency is due to the nature of the fiber electrodes and the absence of heat generation in the battery cells during charge. After hydrogen evolution the regulator current changes, not only in magnitude, but in direction. The electrochemical reaction of oxygen consumption ceases and hydrogen consumption begins. Hydrogen evolves with nearly 100% efficiency on over-charge of the negative, therefore hydrogen dominates in the battery atmosphere. The regulator's polarity remains the same, i.e. the cadmium electrode is negative and the gas electrode is positive. In conjunction with electrochemical hydrogen consumption, oxygen is consumed chemically with hydrogen at the hydrogen electrode and cadmium electrode.

The complex nature of the pressure curve is a result of the different rates of hydrogen-oxygen production and consumption. The falling pressure after hydrogen evolution occurs due to the high rate of electrochemical and chemical reactions as a result of an optimal amount of hydrogen-oxygen mixture. A stationary pressure plateau follows when the rate of electrochemical reaction equals 22 A. This indicates the rate of chemical reaction (hydrogen-oxygen consumption) is equal to 17 A because the total rate of hydrogen production equals 39 A (10 cells 3.9 A per cell). Discharge capacity equals 96 Ah, indicating a high charge efficiency of the nickel oxide electrode.

Fig. 4 displays the same parameters as Fig. 3, however the initial current is 100 A. We can charge to the same state-of-charge in a shorter period of time while delivering full battery capacity. Fig. 5 illustrates the charge characteristics of the CVM at 40 °C. Hydrogen is produced during float charge because the average battery voltage is equal to 1.58 V per cell, however, all hydrogen is consumed in chemical reaction and only oxygen current was recorded according Fig. 5. The maximum value of oxygen consumption is 84 A, including electrochemical and chemical reactions. Calculation of charge efficiency on the basis of experimental data indicates that charge at float current is equal to 3.9 A and is not effected at this temperature. The majority of heat is generated in the

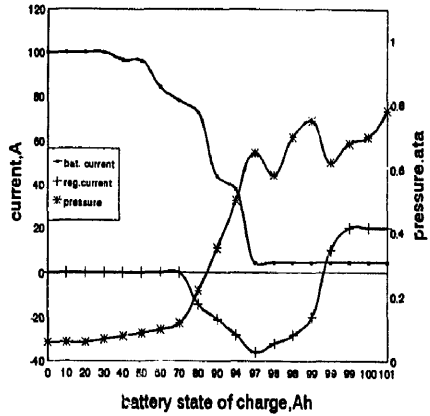


Fig. 4. Charging characteristics at 25 °C: pressure, battery current, and regulator current vs. state-of-charge. Initial charge current = 100 A, and discharge capacity = 96 Ah.

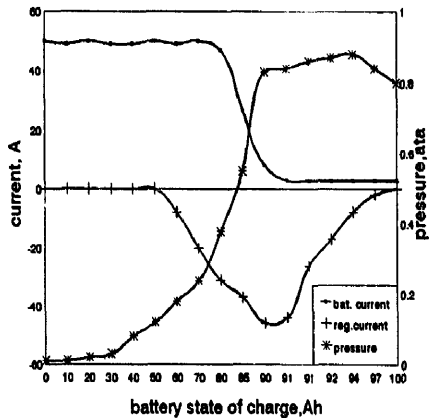


Fig. 5. Charging characteristics at 25 °C: pressure, battery current, and regulator current vs. state-of-charge. Initial charge current = 50 A, and discharge capacity = 83 Ah.

regulator and heat distribution can be calculated between the regulator and battery cells by means of Eq. (6).

Heat dissipation in the battery cells at 40 °C charge is 40 W at 88 Ah state-of-charge. The heat is equal to 100.9 W dissipates in the regulator: 49.5 W as a result of electrochemical oxygen consumption and 51.4 W as a result of chemical oxygen consumption at the cadmium electrode of the regulator.

5. Conclusions

The CVM battery is a new battery design employing vented cells in a sealed, maintenance-free battery configuration.

The CVM design differs from the individual sealed cells or the low maintenance nickel–cadmium batteries because it operates in terms of a complete battery. In terms of the total battery: the individual battery cell contributes only to the battery's operation through the common gas space. Preliminary results from the 100 Ah prototype Ni–Cd battery demonstrates the unique capability of the battery design. Furthermore, the CVM concept should, in principal, be applicable to other aqueous battery chemistries.

The CVM battery could find applications in electric vehicles, stand-by power systems, submarines, and other high voltage, high capacity applications.

References

- [1] *US Patent No. 5290640* (1994).
- [2] M. Anderman and B. Tsenter. *Proc. 10th Annual Battery Conf. Application and Advances, Long Beach, FL, USA, 1994*, pp. 141–146.
- [3] B. Tsenter and N. Lyzlov, *Metal–Hydrogen Electrochemical Systems*, Chimia, Leningrad, 1989, p. 282.
- [4] A. Bard, D. Parsons and J. Jordan (eds.), *Standard Potentials in Aqueous Solution*, IUPAC, 1985, p. 836.
- [5] D.D. Macdonald and M.L. Challingsworth, *J. Electrochem. Soc.*, **140** (1993) 606.