

PERFORMANCE ANALYSIS OF ZINC-BROMINE BATTERIES IN VEHICLE AND UTILITY APPLICATIONS

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Summary

Rechargeable zinc-bromine batteries exhibit a number of inherent advantages that let them appear as possible candidates for applications in electric vehicles and utility load levelling. Based upon known single cell data, the performance characteristics of zinc-bromine batteries in vehicle and utility applications are predicted. The attainable specific energy and energy efficiency are computed as a function of specific power. The effects of specific cell resistance, self-discharge rate, and charge and discharge time on specific energy and efficiency are examined.

Introduction

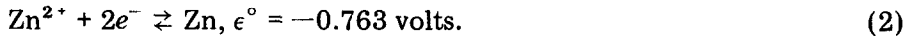
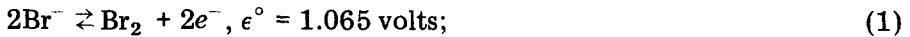
Some of the inherent advantages of the zinc-bromine battery are that it is based upon the use of abundant and relatively inexpensive reactants, is capable of attaining high specific energy values and efficiencies, and operates at, or near, normal temperature. These principal advantages have led to the recent increase of attention that zinc-bromine systems are receiving. Several new approaches to zinc-bromine batteries have been taken in different laboratories [1 - 7].

This paper is aimed at predicting the performance characteristics of the zinc-bromine battery employing a cation exchange membrane as the separator. This system has been investigated extensively, and sufficient experimental data are available [5 - 7] to allow a prediction of systems energy efficiency and specific energy as a function of specific power. The former quantity is of particular interest for load levelling applications whereas the specific energy relation is more pertinent to vehicle applications. Some of these aspects have been presented in less detail in an earlier comparative analysis of the zinc-bromine and zinc-chlorine systems [8].

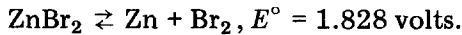
Qualitative systems description

A schematic diagram of the system discussed here is shown in Fig. 1. It uses a cation exchange membrane to separate the zinc electrode from the bromine electrode compartment. This avoids the precipitous self-discharge which would otherwise result from zinc reacting chemically with bromine whose solubility in concentrated bromide solutions can be as high as 40% by weight [5]. The high solubility allows bromine to be conveniently stored in a container as dissolved bromine. During discharge, bromine-containing zinc bromide solution is pumped past an inert carbon electrode, resulting in the reduction to bromide or, more precisely, tribromide ions. A second pump circulates zinc bromide solution past another carbon electrode, carrying a Zn layer, which is anodically oxidized to zinc ions.

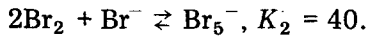
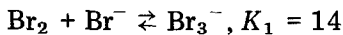
During charging, bromine is formed at the positive electrode and zinc deposited onto the negative electrode. The pertinent electrode reactions are:



Summation of the above equations yields the cell reaction:



With the exception of the nearly fully charged condition, most of the bromine is present as the complex tribromide and pentabromide ions [9] according to



Near the fully charged condition, the zinc bromide concentration is lowest, and the bromine solubility quite low [5]. Hence, some bromine is present in a second liquid phase as elemental bromine.

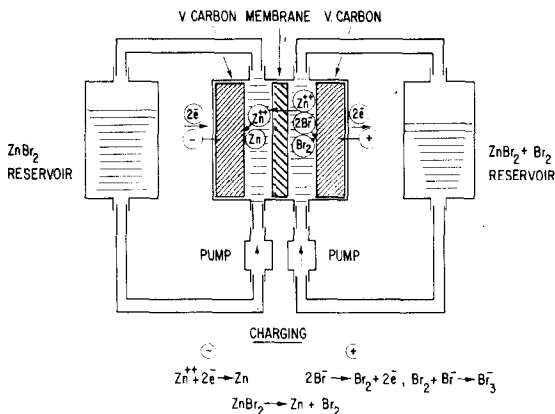


Fig. 1. Schematic diagram of zinc-bromine system.

Residual diffusion of bromine or tribromide through the ion exchange membrane leads to self-discharge whose rate is strongly dependent on the membrane equivalent weight and thickness [10]. For a given membrane, the rate of self-discharge increases during cell charging as the bromine concentration in the positive electrode compartment increases.

Experimental inputs and assumptions

For the operating range of interest and circulated solutions, the current-voltage curves of zinc-bromine cells are found [6, 7] to be essentially linear and determined by the ohmic resistances of electrolyte and membrane. The following analysis is based on the use of Nafion[®] (Du Pont de Nemours) perfluorosulfonic acid cation exchange membranes types 120 and 125 with fixed equivalent weight 1 200 and thicknesses of 0.3 and 0.1 mm, respectively. Both the resistivity of, and the Br₂ diffusion rate through, a given membrane depend on electrolyte composition and Br₂ concentration [6, 10]. Hence, the cell resistance and the self-discharge rate change during charging and discharging. Instead of considering these time-dependent changes, averages of the experimentally observed cell resistances and self-discharge rates [5, 6] were employed in the present analysis. Furthermore, the cell voltage changes in accordance with the Nernst equation as the reactant and the electrolyte concentrations change [6]. This results in a shifting of the straight-line polarization curves to the extent of 0.1 V, and in a change in slope of the order of 15%. Instead of describing these changes by appropriate functional relationships, the analysis is based on the curves shown in Fig. 2 which represent the time average of the cell voltage during charge and discharge as a function of the current density. An economic optimization of the zinc-bromine battery for utility load levelling in terms of membrane thickness and equivalent weight has been considered elsewhere. In that analysis, the time-variation of electrolyte concentration and self-discharge current was taken into account [11].

The linear cell polarization curves shown in Fig. 2 apply to specific cell resistances of 4 and 8 Ω cm². Nafion 125 membrane applies to the former case and contributes 2 Ω cm² to the total value of 4 Ω cm², whereas the thicker Nafion 120 membrane contributes 6 Ω cm² to the second case of 8 Ω cm². In both cases, the electrolyte of thickness 2 mm and average resistivity of 10 Ω cm contributes 2 Ω cm². With regard to self-discharge, Nafion 125 membrane results in an average self-discharge current density of 0.7 mA/cm², and Nafion 120 membrane in the proportionately lower value of 0.23 mA/cm².

The analysis uses a maximum reasonable zinc bromide concentration swing from 10% (charged state) to 40% (discharged state) by weight. The possible presence of supporting electrolytes, solvent transport through the membrane, the usually small energy requirements for pumping, the small amount of H₂ evolution [5], and cell self-discharge *during open circuit* were

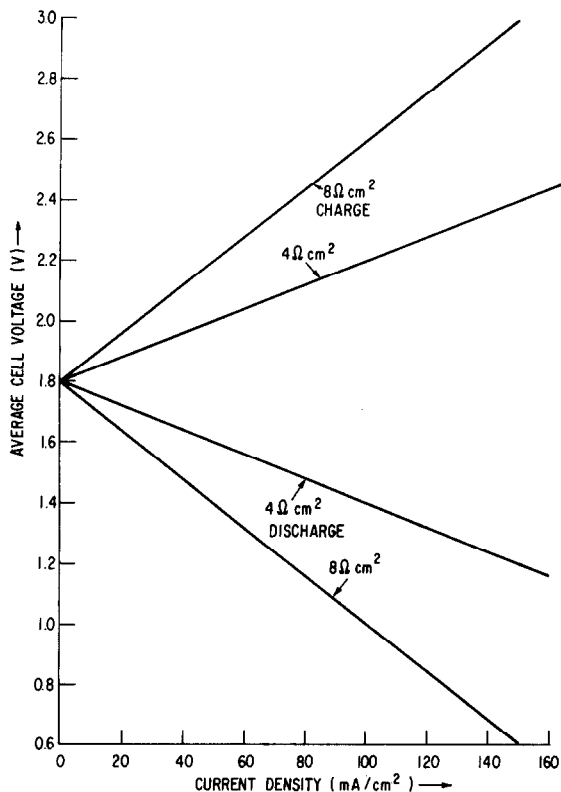


Fig. 2. Current density-average cell voltage curves for charge and discharge for specific cell resistances of 4 and 8 $\Omega \text{ cm}^2$.

neglected. Accessory weights, such as electrode substrates, cell housings, containers, and pumps were not accounted for. However, the weight of all reactive components, that is reactants and zinc bromide electrolyte, was considered. Therefore, the analysis establishes limiting values for efficiency and specific energy and power which have to be reduced in a practical system in proportion to the weight of non-reactive to reactive components.

Analysis

The observed ohmic behavior of zinc-bromine cells and the use of time-averages for electrolyte and membrane conductivity, self-discharge current, and cell voltage allow a greatly simplified mathematical analysis while having a minor effect on the numerical evaluation.

Time-averaged cell performance

For cells showing ohmic behavior, as in Fig. 2, the voltages, V_d on discharge, and V_c on charge, can be expressed as

$$V_d = V_o - ri, \quad (1a)$$

and

$$V_c = V_o + ri \quad (1b)$$

respectively, where V_o is the open circuit voltage, r is the specific cell resistance, and i is the *absolute* value of the externally measurable current density. Since V is always positive, the *absolute* value of the power density, p , is given by

$$p = Vi. \quad (2)$$

In text and figures, p_d refers to the cell on discharge and p_c to the cell during charge. The rate of the self-discharge reaction can be expressed by a self-discharge current density i_{SD} . Then the current density effectively depositing Zn during charging is less than the external current density, i , likewise, the current density effectively discharging the Zn electrode is larger than the external current density. We designate the absolute value of the effective current density as zinc partial current density, i_{Zn} , which is related to i and i_{SD} during discharge and charge, respectively, by

$$i_{Zn,d} = i + i_{SD} \quad (3a)$$

$$i_{Zn,c} = i - i_{SD}. \quad (3b)$$

In this paper, time average values for V_o , r , and i_{SD} are assumed to apply during discharge and charge. Further, cell performance will be considered for constant power discharge and constant current charge conditions. Under the assumption of constant average cell properties, both constant power and constant current conditions are equivalent to a constant external current density or a constant zinc partial current density. Then the energy per unit of stored charge, with the dimension of volts, available during discharge or required during charge, is given by

$$V' = \frac{p}{i_{Zn}}. \quad (4)$$

From the preceding equations, the voltage, zinc partial current density, and energy per unit of stored charge, can all be obtained in terms of the power density. For discharge, these quantities will be double-valued, corresponding to the high (upper sign) and low (lower sign) voltage branches of the discharge power density–voltage relation (*cf.* Fig. 3). The relevant expressions during discharge are

$$V_d = \frac{V_o \pm (V_o^2 - 4rp_d)^{1/2}}{2} \quad (5a)$$

$$i_{Zn,d} = \frac{V_o \pm (V_o^2 - 4rp_d)^{1/2}}{2r} + i_{SD} \quad (6a)$$

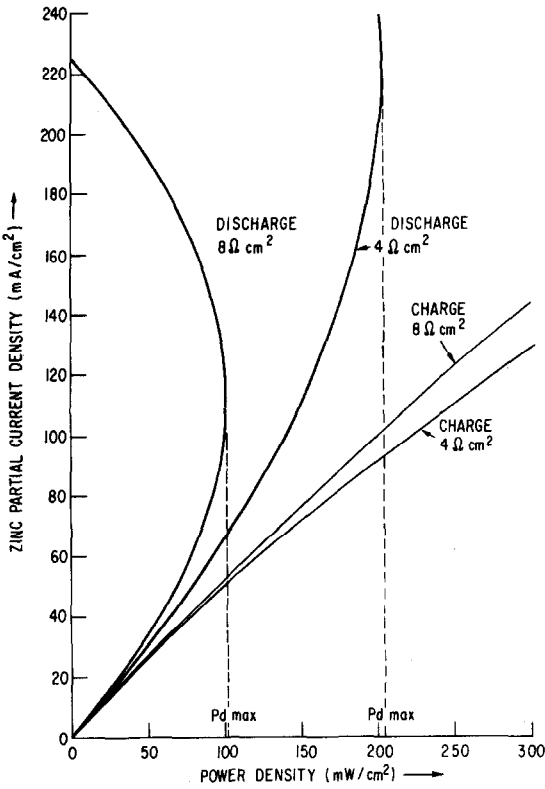


Fig. 3. Zinc partial current density as a function of power density on charge and discharge for 4 and 8 $\Omega \text{ cm}^2$ specific cell resistance.

$$V'_d = \frac{p_d}{\frac{V_o \pm (V_o^2 - 4rp_d)^{1/2}}{2r} + i_{SD}} \quad (7a)$$

where p_d may have any value in the range

$$0 \leq p_d \leq \frac{V_o^2}{4r}. \quad (8a)$$

During charge, the corresponding expressions are

$$V_c = \frac{V_o + (V_o^2 + 4rp_c)^{1/2}}{2} \quad (5b)$$

$$i_{Zn,c} = \frac{-V_o + (V_o^2 + 4rp_c)^{1/2}}{2r} - i_{SD} \quad (6b)$$

and

$$V'_c = \frac{p_c}{\frac{-V_o + (V_o^2 + 4rp_c)^{1/2}}{2r} - i_{SD}} \quad (7b)$$

where p_c may have any value in the range

$$(V_o + ri_{SD})i_{SD} \leq p_c \leq \infty. \quad (8b)$$

Mission-oriented battery performance

Equations (1) - (8) describe single cell performance averaged over the time of complete charge or discharge. These equations apply without regard to the duration of charge and discharge or the amounts of Zn and Br₂. However, battery application for a specific purpose requires additional parameters to be given, with values specific to the application at hand such as electric vehicles or load levelling. Nominal discharge time at some nominal discharge power, maximum discharge power, as well as charging current and time, are among these mission-oriented parameters. In this paper, we chose two such parameters, namely, the nominal discharge time, τ_d , and the reserve power ratio, ν , as particularly pertinent for vehicle and utility applications. The latter is the ratio of the maximum power density attainable on discharge, p_{dmax} , to the nominal power density during discharge, p_{dnom} . Nominal discharge conditions then consist of operating for a time τ_{dnom} at a power density of p_{dnom} , with the option of operating at other power densities, up to the value of p_{dmax} representing an increase in power density by a factor of ν . Operation at p_{dmax} would be possible for a time τ_{dmax} , which is less than τ_{dnom} . Since average values for V_o and r have been employed, p_{dmax} is just $V_o^2/4r$, as indicated by the inequality of eqn. (8a).

From eqn. (6a), the zinc partial current density at nominal power density during discharge can be obtained as

$$i_{Zn,dnom} = i_{SD} + \frac{V_o}{2r} \left[1 - \left(1 - \frac{1}{\nu} \right)^{1/2} \right]. \quad (9)$$

Note that this is the lower of the two possible values of $i_{Zn,d}$ at p_{dnom} , corresponding to the higher voltage on discharge. For transfer of the same amount of zinc, the discharge time, τ_d at any other power density can be determined from the relation

$$i_{Zn,d} \tau_d = i_{Zn,dnom} \tau_{dnom} \quad (10a)$$

where $i_{Zn,dnom}$ is given by eqn. (9) and the two possible values for $i_{Zn,d}$ are given by eqn. (6a). Thus, plots of τ_d or $p_d \tau_d$ vs. p_d can be constructed over the range specified by eqn. (8a).

Average values of V_o , r , and i_{SD} 's imply some range of electrolyte concentrations between the charged and discharged states. This range is dictated by physical factors such as bromine solubility and membrane conductivity, as discussed in the preceding Sections. With a concentration range fixed, the total mass, m , of solvent plus reactants, required to deposit one mole of Zn during charge can be calculated readily. The specific energy on discharge is then given by

$$W'_d = \frac{2F}{m} V'_d \quad (11)$$

where F is the Faraday and V'_d is either of the two possible values for the energy per unit of stored charge from eqn. (7a). The specific power on discharge is given by

$$P'_d = \frac{W'_d}{\tau_d} \quad (12)$$

where τ_d is the discharge time obtained through use of eqn. (10a). Thus, by considering various values for p_d within the range specified by eqn. (8a), plots of W'_d vs. P'_d can be constructed.

Since charging at constant current density is equivalent to the condition of a constant zinc partial current density, eqn. (6b) indicates that power density can be used to specify battery conditions during charge. Repetitive discharge/charge cycles require that the zinc transferred during charge must equal that transferred during discharge. The charge time, τ_c , at any power density, p_c , can then be determined from the relation

$$i_{Zn,c} \tau_c = i_{Zn,dnom} \tau_{dnom} \quad (10b)$$

where the single value for $i_{Zn,c}$ is given by eqn. (6b). Conversely, the power density during charge can be obtained for any value of charge time by substitution of eqns. (6b) and (9) into (10b), and rearrangement.

Using the energy per unit of stored charge required during charging from eqn. (7b) and the energy per unit charge delivered during discharge from eqn. (7a), the overall electrochemical energy efficiency, η_w for a complete discharge/charge cycle is given by

$$\eta_w = \frac{V'_d}{V'_c} \quad (13)$$

Thus, for any value of charge time, plots of η_w vs. either p_d or P'_d can be constructed within the range of p_d specified by eqn. (8a).

Results and discussion

Current density–power density relation

The linear current–voltage curves of Fig. 2 lead to the expected parabolic relation between current and power density as expressed by eqns. (6a) and (6b) and shown in Fig. 3. For the two cases of 4 and 8 $\Omega \text{ cm}^2$ specific cell resistance, maximum discharge power densities, p_{dmax} , of 202 and 101 mW/cm^2 are obtained at current densities of 226 and 113 mA/cm^2 , respectively. However, sustained power levels in excess of half of these values are unfeasible, since the pumping rates for the electrolytes needed to avoid concentration polarization at the two electrodes would become unreasonably large. On charging, the input power density rises monotonically with increasing current density. While the curves in Fig. 3 have been shown for charging current densities up to 150 mA/cm^2 , long-term charging at values much in excess of 50 mA/cm^2 has to be avoided owing to the undesirable formation

of dendritic zinc layers [5] unless effective dendrite inhibitors are employed. A current density of 50 mA/cm^2 corresponds to an input power density of 100 and 95 mW/cm^2 for the $4 \text{ } \Omega \text{ cm}^2$ and $8 \text{ } \Omega \text{ cm}^2$ cases, respectively.

Plotted in Fig. 3 is the zinc partial current density which is equal to the externally measured current density corrected by the addition (discharge) or subtraction of the self-discharge current density as expressed by eqns. (3a) and (3b). On open circuit, with $i = 0$, the Zn electrode is subject to self-discharge, owing to the chemical reaction with Br_2 after diffusion through the membrane, and as expressed by i_{SD} . Since i_{SD} is only 0.7 and 0.23 mA/cm^2 for the 4 and $8 \text{ } \Omega \text{ cm}^2$ cases, a plot of i vs. p is essentially indistinguishable from the plot of i_{Zn} as shown in Fig. 3.

Cell voltage and energy/stored charge

The cell voltage is also related parabolically to the power density, as expressed by eqns. (5a) and (5b) and shown in Fig. 4. Maximum power densities are obtained at half cell voltage. As mentioned before, sustained

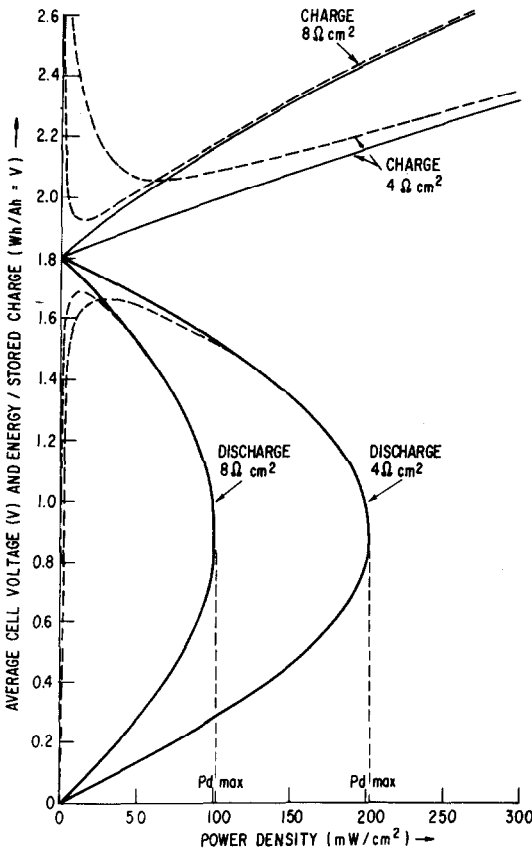


Fig. 4. Average cell voltage (solid lines) and energy/stored charge or power density/zinc partial current density (dashed lines) vs. power density on charge and discharge for 4 and $8 \text{ } \Omega \text{ cm}^2$ specific cell resistance.

operation near the power density maximum is unfeasible. At reasonable power density levels of 100 mW/cm^2 for a specific cell resistance of $4 \Omega \text{ cm}^2$ and 50 mW/cm^2 for $8 \Omega \text{ cm}^2$, a cell voltage of 1.5 V is achieved in both cases. On charging with a power density of 100 mW/cm^2 , corresponding to a reasonable current density of approximately 50 mA/cm^2 , the cell voltages are 2 V and 2.17 V for the 4 and $8 \Omega \text{ cm}^2$ specific cell resistances, respectively.

The broken curves in Fig. 4 signify the power density/zinc partial current density according to eqns. (7a) and (7b) or, alternatively, the energy/stored charge which has the units Wh/A h or volts. If there were no energy losses due to self-discharge and hydrogen evolution, the cell voltage (solid curves) would properly express the energy (Wh) that has to be expended during charging to produce a certain zinc layer thickness or stored charge (Ah) or, conversely, the energy that is produced during discharge of a zinc layer of certain thickness. However, the energy losses from self-discharge and other processes cause the energy input per unit of charge to be smaller during discharge. The effect of the self-discharge rate is pronounced only at low power densities, when the self-discharge current density, i_{SD} , becomes significant with respect to the external current density, i .

The cases of 4 and 8 ohm cm^2 in Fig. 4 correspond to the use of membranes with 0.1 and 0.3 mm thickness, respectively. Use of the thinner membrane results in lower specific cell resistance and higher power densities on discharge, but at the sacrifice of higher self-discharge rates. At low power densities, the self-discharge effect overwhelms, and it would be preferable to use the thicker membrane. However, for practically interesting power densities above 60 mW/cm^2 on charging and above 25 mW/cm^2 on discharging, ohmic effects are over-riding and the use of the thinner membrane is preferable. An optimum choice of the membrane would involve an optimization of the energy efficiency in terms of both the membrane thickness and its equivalent weight.

Effect of discharge time on power and energy density

The foregoing considerations on single cell characteristics apply without regard to charge and discharge times or reactant amounts. However, practical applications of batteries in electric vehicles and load levelling require the delivery of a specified amount of stored energy or of certain power levels for specified lengths of time. Typically, it is desired to operate the battery for a nominal discharge time, τ_{nom} , at a nominal power level, p_{dnom} , which is only a fraction of the maximum power density, p_{dmax} . This results in a power reserve ratio $p_{\text{dmax}}/p_{\text{dnom}}$ which is essential, for example, for vehicle acceleration.

Once the nominal discharge power (or power reserve ratio) and the discharge time have been specified, the entire curve relating power density to discharge and charge time is established. The relationship between energy density (here defined as energy per unit area with dimensions Wh/cm^2) and discharge time is identical to a plot of $p_{\text{d}}\tau_{\text{d}}$ vs. the discharge time, τ_{d} . Two

different cases will be considered in detail; the first corresponds to typical electric vehicle and the second to load levelling applications.

Shown in Fig. 5 is the effect of discharge time on power and energy density for a power reserve ratio of 4 and a nominal discharge time of 2 hours, a case most pertinent to *electric vehicle applications*. Curves are plotted for the cases of 4 and 8 $\Omega \text{ cm}^2$ specific cell resistance, with the solid line representing the power density and the dashed lines the energy density. Since the *maximum* power densities according to Fig. 4 are 200 and 100 mW/cm^2 for these two cases, the *nominal* power densities are 50 and 25 mW/cm^2 for the nominal discharge time of 2 hours. Discharge at higher power levels leads to more than a proportionate decrease in discharge times. Thus, a doubling of the power density results in a discharge time of 56 min, and quadrupling (power maximum) in a discharge time of only 16 min. Cell shorting ($p = 0$) leads to discharge in 8 min for both 4 and 8 $\Omega \text{ cm}^2$ specific cell resistance, since the 4 $\Omega \text{ cm}^2$ cell stores a nominal energy density of 100 mWh/cm^2 as compared with 50 mWh/cm^2 for the 8 $\Omega \text{ cm}^2$ cell.

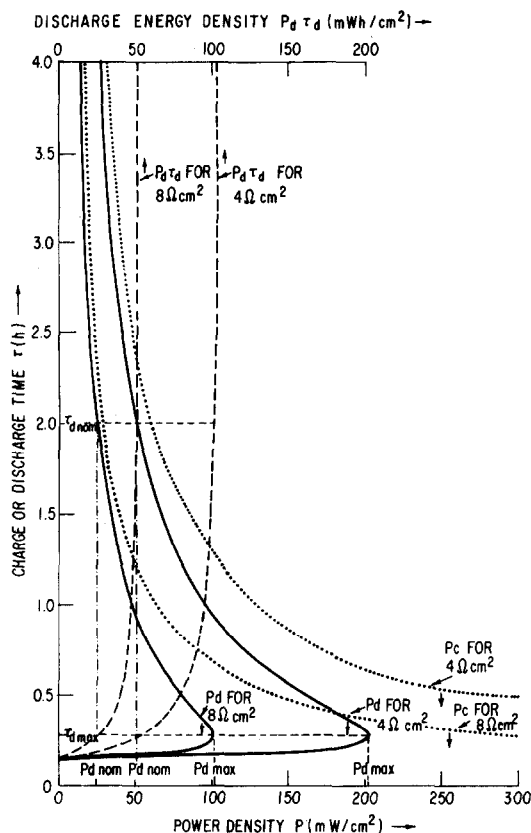


Fig. 5. Power (p_c and p_d) and energy density ($p_d \tau_d$) as a function of charge and discharge time for power reserve ratio $p_{d\text{max}}/p_{d\text{nom}} = 4$, and nominal discharge time 2 h (electric vehicle case).

The energy density is essentially independent of discharge time from 1.5 to 4 hours. However, for discharge times smaller than 1 hour, the delivered energy density decreases steeply, attaining only 80% of the nominal energy for a 0.5 h discharge and 55% for discharge at the maximum power density. The curves in Fig. 5 represent optimum discharge times, which cannot be fully attained in practical cells. Especially for power densities near the maximum, the discharge times will be smaller due to: (1) insufficiently fast transport of bromine to the electrode, especially toward the end of discharge when the bromine concentration is at a minimum; (2) the commonly observed presence of some zinc on the electrode substrate which cannot be anodically discharged at sufficiently high rates. This effect is also particularly pronounced toward the end of discharge when only a small amount of zinc remains on the surface, and could be due to non-uniform current distribution across the surface or different energetics for zinc next to the carbon substrate as compared to bulk zinc.

On charging the zinc-bromine battery, the power density rises monotonically with decreasing charging times. This is illustrated by the dotted curves in Fig. 5. To prevent the formation of zinc dendrites, charging at current densities above 50 mA/cm has to be avoided. This corresponds to maximum feasible power densities of 100 and 95 mW/cm² for the 4 and 8 Ω cm² cases, and a minimum charge time of 1.25 h for the 4 Ω cm² and 0.75 h for the 8 Ω cm² case.

In the *load levelling case*, a power reserve ratio of 2 and a nominal discharge time of 4 hours were chosen. This corresponds to nominal power densities of 100 and 50 mW/cm² and nominal energy densities of 400 and 200 mWh/cm² for the 4 and 8 Ω cm² cell resistance case, respectively. Figure 6 illustrates the relation between discharge time and power and energy density. Discharge in 8 h leads to power densities of 54 and 27 mW/cm² and energy densities of 440 and 200 mWh/cm². Discharge at the maximum power density has a maximum duration of 1.2 h but the attainable energy densities are only 60% of the nominal values. Cell shorting leads to complete discharge in 35 min.

Charging at a maximum feasible current density of 50 mA/cm² again corresponds to power densities of 100 and 95 mW/cm² for the 4 and 8 Ω cm² cases or to minimum charging times of 5.4 and 3 h. A more reasonable charging time of 6 h leads to power densities of 90 and 45 mW/cm² or current densities of 45 and 25 mA/cm² for specific cell resistances of 4 and 8 Ω cm².

For specified systems output power and energy and identical discharge times, twice the total electrode area is required for the cell with 8 Ω cm² specific resistance as compared to that with 4 Ω cm². This simple rule does not apply to the region below the power maximum in Figs. 5 and 6 which, however, is not a practical operating region.

Specific energy-specific power relation

This relation is of considerably larger interest to electric vehicle than to load levelling applications. Computation of this relation involves, in addition

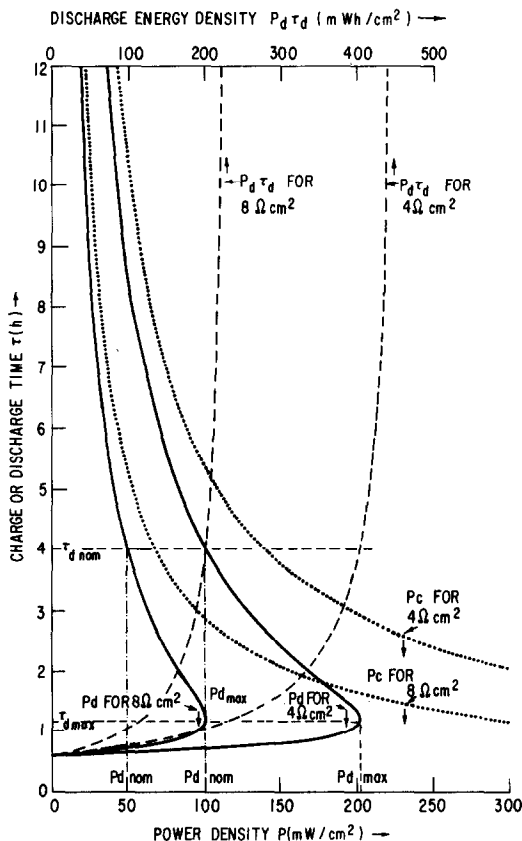


Fig. 6. Power (p_d and p_c) and energy density ($p_d \tau_d$) as a function of charge and discharge time for power reserve ratio 2 and nominal discharge time 4 h (load levelling case).

to the specification of a power reserve ratio and a nominal discharge time, the choice of a reasonable zinc bromide concentration swing. While the *reacting* amount of zinc bromide yielding the reactant amounts of zinc and bromine is already given by any pair of values of power density and discharge time, the choice of zinc bromide concentrations in the fully charged and discharged condition was left open in the foregoing discussion and figures.

For this analysis, a zinc bromide concentration swing between 10% in the fully charged condition and 40% by weight in the fully discharged condition was assumed. Within this concentration swing, the electrolyte conductivity and the zinc deposit morphology are acceptable [5, 6]. The power reserve ratio was again chosen as 4 and the nominal discharge time as 2 h. Since no accessory weights were considered, the values for specific energy and power computed from eqns. (11) and (12) constitute limiting values which must be reduced in relation to the weight of accessories compared with that of reactants and electrolyte.

Specific energy-specific power curves for zinc-bromine systems for membranes with two different thicknesses (0.1 mm corresponding to $4 \Omega \text{ cm}^2$ and 0.3 mm to $8 \Omega \text{ cm}^2$) are shown in Fig. 7. The specific cell resistance has

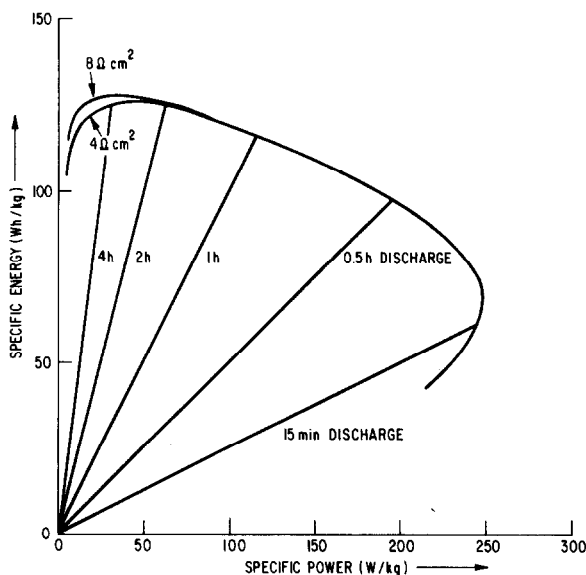


Fig. 7. Specific energy *vs.* specific power for zinc-bromine systems with power reserve ratio 4 and nominal discharge time 2 h (vehicle case) showing effect of discharge time for 4 and $8 \Omega \text{ cm}^2$.

very little effect on the attainable specific power value. The lower power densities that correspond to the larger specific cell resistance according to Fig. 5 are compensated for by increasing the electrode area accordingly. In a practical system, however, this results in a considerable penalty in cost and some penalty in specific power, since the weight of the non-reactive cell components has to be increased.

A maximum specific power of value 245 W/kg is obtained with a corresponding specific energy of 75 Wh/kg. Discharge at the power maximum is possible for 17 min, as is also evident from Fig. 5. At the nominal discharge rate of 2 h at 1/4 maximum power output, that is, at 60 W/kg, a limiting specific energy value of 125 Wh/kg is achieved. For a 1 h discharge rate, the specific power is 116 W/kg and the specific energy 116 Wh/kg. The decrease of specific energy at very low values of the specific power results from cell self-discharge which is more pronounced for the thinner membrane equivalent to the $4 \Omega \text{ cm}^2$ case.

Energy efficiency

While specific energy is the more significant quantity for vehicle applications, optimum energy efficiency is the more important consideration for load levelling applications. Also, the power reserve at the operating point may be chosen considerably smaller for load levelling. On the other hand, the discharge times are usually required to be longer. A 4 h discharge at 1/2 maximum power output was chosen as the nominal operating point for this analysis.

The energy efficiency for the zinc-bromine system, calculated from eqn. (13), is plotted in Fig. 8 as a function of the limiting specific power output. Curves are presented for 2-, 4- and 6-hour charge times and apply to specific cell resistances of 4 and 8 $\Omega \text{ cm}^2$. The upper abscissae show the pertinent discharge times as they relate to the specific power values on the lower abscissa.

For the nominal 4-hour discharge, the zinc-bromine system achieves energy efficiencies at 29 W/kg between 65 and 75.5% for charging rates from 2 to 6 h. These values decrease to the range 54 - 63% for a 2 h discharge at 48 W/kg. At the maximum specific power output of 57 W/kg, which can be maintained for a maximum of 1.2 h, the limiting efficiency values are 40 - 45%.

Self-discharge leads to a slight decrease of the efficiency at discharge times larger than 12 h. The more significant effect on energy efficiency is due to the duration of charging. For 6-hour charging, the ohmic losses are considerably smaller than for 2-hour charging, thus raising the energy efficiency by more than 10% over most of the power output range of interest. The effect is larger for an increase in charging time from 2 to 4 h than from 4 to 6 h. For charging times in excess of 6 h, there is only marginal further improvement in the efficiency. The curves plotted in Fig. 8 were computed for a specific cell resistance of 4 $\Omega \text{ cm}^2$. The curves for 8 $\Omega \text{ cm}^2$ are almost identical in the range of specific powers shown. This result is evident from Fig. 4, when energy/stored charge values are compared for 4 and 8 $\Omega \text{ cm}^2$ at identical fractions of the maximum power density. To obtain the same systems specific power output, however, essentially double the electrode area is required for the 8 $\Omega \text{ cm}^2$ case.

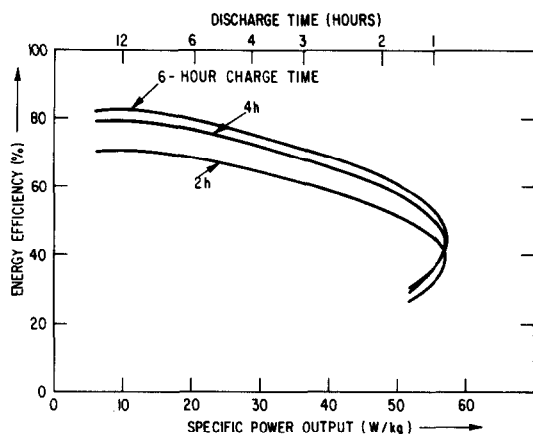


Fig. 8. Energy efficiency vs. specific power for zinc-bromine systems with power reserve ratios 2 and nominal discharge time 4 h (load levelling case) showing effect of charge and discharge time for 4 and 8 $\Omega \text{ cm}^2$.

Conclusions

The zinc-bromine battery, employing a membrane separator and dissolved bromine, is capable of achieving attractive values for the specific energy, specific power, and energy efficiency which make it appear as a possible candidate for electric vehicles and load levelling. The zinc-bromine system can achieve *limiting* specific energies of 124 Wh/kg at 62 W/kg or 1/4 maximum power. In a typical load levelling cycle, that is, 6 hour charge and 4 hour discharge at 1/2 maximum power, the zinc-bromine system can attain energy efficiencies up to 75% at 30 W/kg. The limiting values for specific energy and power do not take into account accessory weights such as electrode substrates, cell housings, pumps, and reservoirs, and have to be reduced in a practical system in proportion to the weight of non-reactive to reactive components.

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