Zinc–bromine battery for energy storage*

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Abstract

The performance of a 2 kW, 10 kW h zinc–bromine battery is reported The battery uses new carbon/PVDF bipolar electrodes and a circulating polybromide/aqueous zinc–bromine electrolyte A turn-around efficiency of 65–70% is achieved Disclosure is also given of an innovative non-flowing-electrolyte cell This system is less complex and, hence, gives increased reliability and a higher return efficiency A 25 A h single cell has completed over 400 cycles (100% depth-of-discharge) with a total return energy efficiency of over 75% Such technology is extremely attractive for remote-area power-supply applications

Introduction

Increasing world-wide awareness of the necessity for efficient energy use and reduced environmental pollution makes research and development into energy storage more important than ever. Battery energy storage provides excellent opportunities for efficient use of oil and coal and for the utilization of pollution-free, but intermittent, renewable energy such as solar, wind, and wave.

Murdoch University is collaborating with Energy Research Corporation (ERC), U S A in developing the zinc–bromine battery for stationary energy storage applications. The technology is particularly attractive because it operates at ambient temperature, performs without penalty under deep-discharge conditions, and has potential for a long cycle life. These characteristics, combined with the projected low cost of battery manufacture ($< \$100$/kW h), make the zinc–bromine battery very attractive for applications such as utility load-levelling; spinning reserve; customer-side load-levelling; remote-area power supplies using renewable energy alone or with diesels in hybrid systems. This paper describes the current status of development of the battery at Murdoch University.

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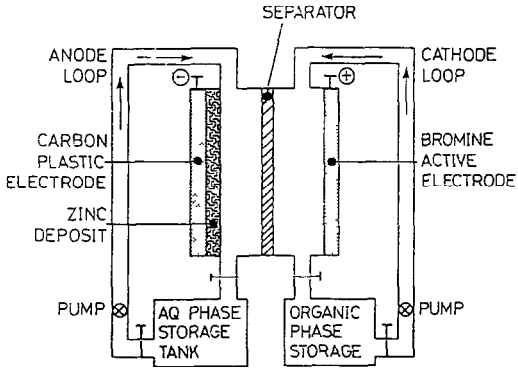

Fig 1 Conceptual diagram of a zinc–bromine cell

Battery concept

The battery stores energy by the electrolysis of an aqueous zinc–bromide salt solution to zinc metal and dissolved bromine Zinc is plated as a layer on the electrode surface while bromine is extracted from the electrolyte with an organic complexing agent On discharge, the zinc and bromine are consumed, regenerating the zinc–bromide salt.

The reactions involved in the battery process are as follows·

$$Zn(s) + Br_2(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Zn^{2+}(aq) + 2Br^-(aq) \quad (1)$$

The function of the complexing reagent is to lower the concentration of bromine in the catholyte by extracting bromine into a water-immiscible phase that acts as a bromine storage medium. This allows high energy storage capacity at a low rate of self discharge The latter results from the diffusion of bromine across the separator from the cathode to the anode compartment The current ERC/Murdoch technology uses certain quaternary ammonium salts to extract bromine as polybromides into an oil-like phase. The use of propionitrile, patented [1] by Murdoch University, is also being investigated

The battery consists of a stack of flow frames into which bipolar electrodes are bonded The electrolyte is circulated into the stack from two storage tanks (anolyte and catholyte) and directed over the electrode surfaces by channels in the flow frames The anolyte and catholyte fluids are separated by a porous membrane. A schematic diagram of the battery system is shown in Fig 1

A battery system having any desired voltage/current characteristic can be fabricated by stacking an appropriate number of the bipolar electrodes together and connecting stacks in various series and/or parallel configurations

Research and development status

Over the years, the researchers at Murdoch and ERC have addressed several issues relating to cost and performance of the zinc–bromine battery.

A new carbon/PVDF bipolar electrode has been developed that provides not only the desired stability in the bromine-rich electrolyte, but also has sufficient flexural strength A low-cost, proprietary material, carbon felt, has been optimized to achieve highly reproducible low overvoltages for the bromine electrode reaction. Several commercially available PVC materials have been screened for their suitability, and material has been selected for fabricating the electrode frames Through extensive studies, the battery electrolyte composition has been optimized to achieve zinc loadings of up to 200 mA cm^{-2} This parameter has a strong bearing on the cost of the battery, as less stack components per kW h storage capacity are needed With the same objective, the size of the electrode has been increased from 872 cm^2 to 1500 cm^2 The design of the flow frame has been improved to achieve uniform electrolyte distribution over the area of the electrode at the lowest possible pressure drop and shunt current loss. Systems for automatic operating and control have been developed State-of-charge, electrolyte pH, and electrolyte levels are parameters that can now be automatically monitored The polybromide/aqueous electrolyte mixer loop, previously required to achieve efficient bromine exchange between the bromine-rich polybromide and the aqueous electrolyte, has been replaced by a specially designed catholyte storage tank. This has not only improved the reliability, but also the cost and efficiency of the battery

Circulating electrolyte battery

A 2 kW, 10 kW h battery that incorporates all the developments discussed above is currently under test and evaluation at Murdoch University. The specifications are listed in Table 1. This unit can be seen as a module for batteries of larger size. The system consists of 30 cells with 1500 cm^2 electrodes arranged in a bipolar configuration. The electrolyte is supplied from two separate tanks to the positive and negative cell sides The battery can be charged and discharged at various rates. The effect of current density on battery efficiency is shown in Fig. 2 A typical charge/discharge curve for the battery is shown in Fig 3.

The battery is self-contained and operates without auxiliary power. The d c motor pumps are powered from the stack and their speed is controlled through a microprocessor. The charge and discharge cycles are controlled by the charging equipment and the load. The microprocessor regulating the pump-motor speed gives a shut down only if a monitored parameter goes out of range. The latter parameters are electrolyte temperature, electrolyte pump pressures, electrolyte levels in the anolyte and catholyte tanks, and

TABLE 1

Specifications for a 10 kW h circulating electrolyte demonstration zinc–bromine battery

Max constant power	3 kW
Max constant current	60 A
Max. capacity	300 A h, 10 kW h
Energy efficiency	65–70% (>75% projected)

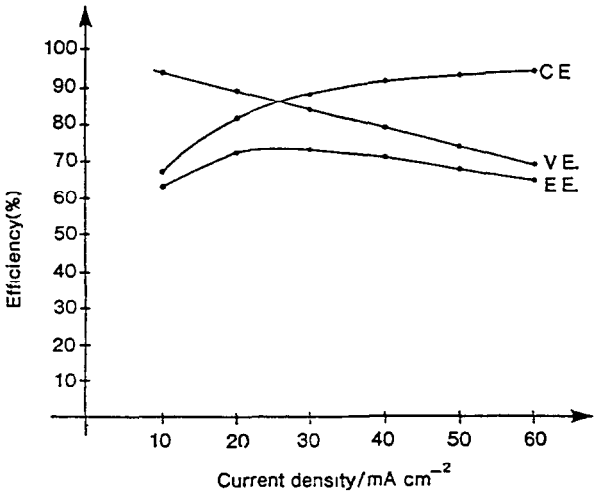

Fig 2 Effect of current density on efficiency

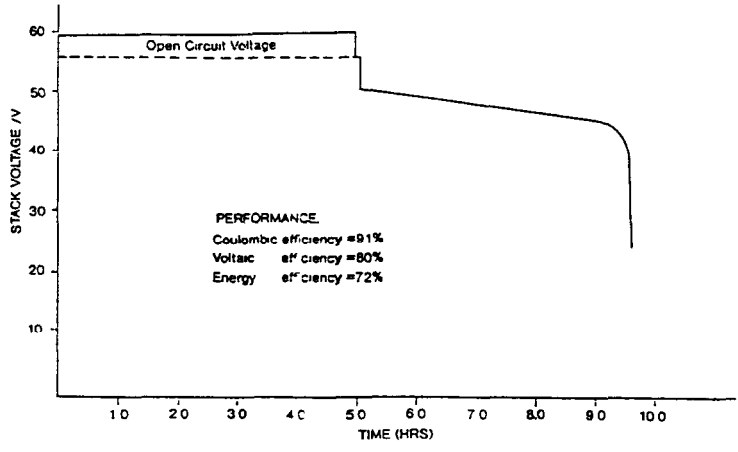

Fig 3 A typical cycle of the 2 kW, 10 kW h battery

stack voltage Provision is also made for continuous monitoring of the state-of-charge and the electrolyte pH.

Taking into account all the auxilliary equipment losses, a turn-around efficiency of 65–70% has been achieved. By improving the coulombic efficiency and lowering the power loss in the pumps, an efficiency of $>75\%$ can be obtained.

Non-flowing electrolyte battery

While circulating-electrolyte zinc–bromine batteries are ideal for high rate, large storage capacity applications, the use of pumps renders them less suitable for small capacity and remote-area applications. Realising this,

very recently, a battery has been designed that does not use the circulating-electrolyte system The battery is less complex in its engineering, giving an increased reliability With no moving components and no losses to other auxiliaries, it also gives a higher return efficiency. A fully sealed 25 A h single cell has already logged over 400 full (100% depth-of-discharge) cycles with a total return energy efficiency of over 75% A typical charge/discharge curve is shown in Fig 4.

Similar results have also been obtained from a 25 A h, 8 cell battery The construction of a 50 A h, 12 V battery is now in progress The specifications for this battery are listed in Table 2 This unit serves as a module for larger size batteries

Except for a recent report by Manassen *et al.* [2], there appears to be no other work on non-circulating-electrolyte zinc–bromine batteries. The exact details of the Murdoch system cannot be disclosed at this stage. The results to date are very encouraging and, hopefully, this battery will become an attractive extension to the circulating-electrolyte technology

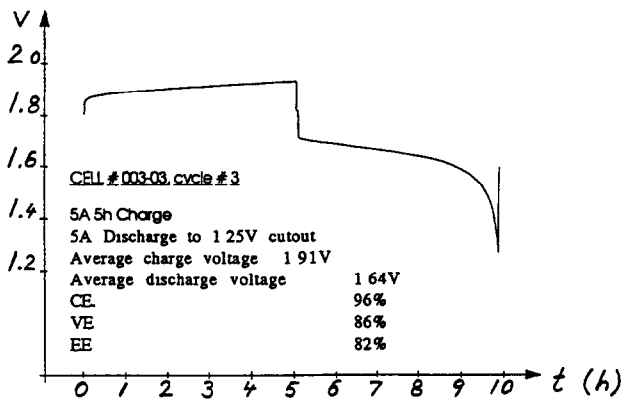

Fig 4 A cycle of a non-flowing-electrolyte cell

TABLE 2

Specifications for a module of a non-circulating-electrolyte battery

Charge voltage	15 V
Av discharge voltage	13 V
Charge current	5 A
Discharge current	5 A
Capacity	50 A h, 600 W h
Coulombic efficiency	92%
Voltaic efficiency	85%
d c–d c energy efficiency	78%
Energy density	30 W h l^{-1}, 25 W h kg^{-1}

References

1 A J Parker, P Singh and J Avraamides, *U S Patent 4 377 623* (1981)
2 J Manassen and I Cabasso, *J Electrochem Soc*, *136* (1989) 579