Halogen: A high-capacity cathode for rechargeable alkaline batteries

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Here we report a new high capacity battery system referred to as RAH batteries, which is based upon a high energy cathode—halogen (such as Br_2 or Cl_2) and metal hydride anode.

The search for higher capacity batteries has focused on a wide range of materials including anode materials,[1] cathode materials[2] and electrolyte.[3] With the considerable increasing attention on electric automobile and portable computers, rechargeable batteries such as nickel/metal hydride[4] (Ni/MH), fuel cell and Li-ion batteries[5] have increased in importance. At the end of 19th century, the commonly used secondary alkaline batteries which are based upon nickel oxide cathodes (Ni/Fe and Ni/Cd batteries) were invented. More recently, the Ni/MH battery has been developed and has increased the energy capacity of nickel oxide batteries. Power, cycle life, and safety factors have led to annual global yields of 1.5 billion nickel batteries. Nickel batteries have been the dominant secondary battery and have continued to be of widespread interest[6] for over a century.[6,7] However, the existent Ni/MH, Ni/Fe and Ni/Cd batteries have two disadvantages: they have low discharge voltage of $1.2 \sim 1.3$ V and their specific energy capacity is largely limited by the charge capacity of nickel oxide cathode (292 mA h g^{-1}). Alternative cathodes, such as AgO or MnO_2, have found only limited applications because of their high cost and lower cycle life.[8] The thermodynamic properties of halogen make it a natural choice for use as a cathode in alkaline batteries, because it can provide higher capacity and potential than a nickel oxide cathode. Moreover, in contrast to nickel, halogen is inexpensive. But they have not been used as cathode materials for aqueous alkaline batteries, the argument being that halogen is highly unstable in alkaline solution. Here we show a new system of rechargeable batteries, rechargeable alkaline halogen (RAH) batteries, which is based upon a halogen cathode. RAH batteries provide high discharge voltage of $1.9 \sim 2.2$ V, high energy capacity of $90 \sim 136$ W h kg^{-1} and a greater than 500 cycle life.

Halogen is a typical nonmetal and its usual valance is -1. It is a strong oxidant, and its redox potential is very high and not affected by the variation of solution pH value. The potential of Br_2 is constant in either alkaline or acidic solution: $E_{Acid}^0(Br_2/Br^-) = E_{Base}^0(Br_2/Br^-) = 1.085$ V. However, the potentials of most metal oxides are influenced by solution acid–base value. For example, the potential of the NiOOH electrode is 1.83 V in 1 M $HClO_4$, while it is only 0.49 V in 1 M KOH. Thus, under the condition of same pH value and anode, the alkaline halogen battery has higher potential than the alkaline nickel oxide battery. For instance, the open-circuit voltage of the alkaline Br_2/MH battery is 1.93 V, however that of the alkaline Ni/MH battery is only 1.33 V. Halogen also has high capacity and electrochemical activity. Here we list the theoretical capacities of the halogen cathodes as follows: F_2 (1400 mA h g^{-1}), Cl_2 (755 mA h g^{-1}), Br_2 (335 mA h g^{-1}).

Although halogen has excellent electrochemical performance, it has not been considered for applications in alkaline batteries because of its high instability in alkaline solution. It is correct on one hand for usual alkaline batteries because these cathodes react with alkali during charge and discharge. For example, the NiOOH cathode discharges in accordance with Eqn. (1):

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \qquad (1)$$

Eqn. (1) means that there must be alkali in the catholyte for the ordinary alkaline batteries. But on the other hand this view is incorrect for the halogen cathode. Essentially halogen does not need alkali joining the charge and discharge reaction. Halogen reacts in accordance with: $X_2 + 2e^- \rightarrow 2X^-$ (X = Cl, Br), so a halogen cathode can be used in alkaline batteries.

Here we show a new battery system referred to as RAH batteries, which is based upon a high energy cathode—a halogen (such as Br_2 or Cl_2) and a metal hydride anode. Highly conductive KOH and KBr (or KCl) are used as anolyte and catholyte respectively separated by a permselective cation exchange membrane. The use of a membrane is particularly important to obtain the stability of our new batteries. Although RAH batteries contain the same MH anode as nickel batteries, they provide a higher discharge voltage of $1.9 \sim 2.2$ V and $>100\%$ more energy capacity.

We find that a certain amount of halogen has a high stability for many days when it is separated from concentrated KOH solution by a permselective cation exchange membrane. Halogen has a low rate of penetration through the membrane when it is transformed into multiple halogen anions (such as Br_3^-, Br_7^- *etc.*). The self-discharge of alkaline MH/Br_2 batteries was measured. The alkaline halogen cells consisted of 60 mg (20 mA h) Br_2 cathodes or 26.5 mg (20 mA h) Cl_2 cathodes, excessive MH anodes, 10 M KOH anolyte and 1 M KBr catholyte. The anolyte and catholyte were separated by carboxyl acid perfluorocarbon cation membrane (Nafion N-961, made by Dupont Co. USA). The cathode current collector was Dimensionally Stable Anode (DSA, RuO_2-TiO_2/Ti, made by Beijing Chemical Machinery Plant, Beijing.) of 3 cm^2. After storing these batteries for different periods, they were discharged to 1.0 V at current density of 1 mA cm^{-2}. The results (Fig. 1) indicate that the self-discharge rate of the alkaline halogen batteries in 10 M KOH electrolyte is evidently lower than that of the existent alkaline Ni/MH battery. After 30 days storage, the capacity retention is 90% and 81% for the alkaline Cl_2/MH and Br_2/MH batteries respectively, while only 65% for the alkaline Ni/MH battery. Obviously, the stability of alkaline halogen battery is very good and attributed to the cation exchange membrane.

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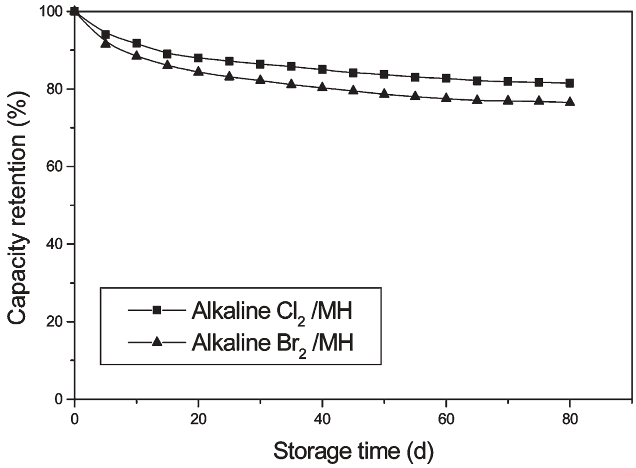

Fig. 1 The self-discharge curves of alkaline halogen batteries.

We developed appropriate halogen cathodes for these systems. The halogen cathodes consisted of 13.2 mg (10 mA h) Cl_2 or 29.9 mg (10 mA h) Br_2 respectively. The area of each cathode was 1.2 cm^2, and the capacity of MH anode was excessive. All cells were discharged to 0.9 V at current density of 1 mA cm^{-2}. The discharge curves (Fig. 2) suggest that the average discharge potential of the Cl_2 cathode (1.35 V) and Br_2 cathode (1.08 V) *versus* standard hydrogen electrode (SHE) is 0.86 V and 0.59 V higher than that of NiOOH cathode (0.49 V) respectively. The specific capacity for the Cl_2 and Br_2 cathodes are 717 mA h g^{-1}(95% of 755 mA h g^{-1}) and 311 mA h g^{-1} (93% of 335 mA h g^{-1}) respectively, both greater than that of 260 mA h g^{-1} (89% of 292 mA h g^{-1}) for NiOOH cathode. The combination of higher efficiency and theoretical capacity leads the halogen batteries to a further increase in comparative energy capacity. Additionally, Cl_2 electrode has higher discharge capacity than Br_2 due to its high redox potential and specific capacity.

In the discharge process of halogen batteries, taking Br_2/MH batteries as example, Br_3^- electrode is reduced to $3Br^-$. In the mean time, MH electrode is oxidized and H^+ is dissociated out, which combines with OH^- to form H_2O. K^+ moves to the cathode through the ion exchange membrane and is associated with Br^-, forming KBr. The reaction is as follows:

$$\text{Anode: } 2MH - 2e + 2OH^- \rightarrow 2M + 2H_2O \tag{2}$$

$$\text{Cathode: } Br_3^- + 2e \rightarrow 3Br^- \tag{3}$$

The charge process of halogen cells is just the reverse. In an alkaline halogen battery, the discharge product from the MH anode is H_2O only, whilst that of the halogen cathode is halogen anion. The discharge reactions may be shown as:

$$2MH + X_2 + 2NaOH \rightarrow 2M + 2NaX + 2H_2O\ (X = Br, Cl) \tag{4}$$

A variety of alkaline halogen batteries were prepared and discharged. The open-circuit potential observed in the alkaline halogen batteries changes within $\pm$ 0.04 V with the variation of environmental conditions such as the electrolyte and halogen concentration. Generally, the alkaline Cl_2/MH potential, at 2.19 V, is 0.274 V higher than the Br_2/MH battery. On the basis of their open-circuit voltages and Eqn. (4), the alkaline Cl_2/MH and Br_2/MH batteries have a respective maximum energy capacity of 459 W h kg^{-1} and 301 W h kg^{-1}, both much higher than the maximum of 235 W h kg^{-1} and 212 W h kg^{-1} for existing alkaline Ni/MH and Ni/Cd batteries.

The energy capacities of RAH batteries was measured at various current densities. Energy capacity is in respect of the total mass of anode, cathode, membrane. The experiment results are shown in Fig. 3. At high current density, the discharge voltage of alkaline Cl_2 batteries is between 1.8 and 2.1 V, and of alkaline Br_2 batteries is between 1.6 V and 1.9 V. The alkaline halogen batteries possess significantly higher energy capacity than the alkaline Ni/MH batteries because of their higher discharge voltage and capacity. In particular, the alkaline Cl_2/MH battery provide energy capacity of 131 W h kg^{-1}, 118% higher than the conventional Ni/MH batteries (60 W h kg^{-1}, ref.1). The energy capacity of Br_2/MH battery is 90 W h kg^{-1}, 50% higher than Ni/MH batteries. The results also suggest that RAH batteries provide higher energy at low current density of 1 mA cm^{-2}.

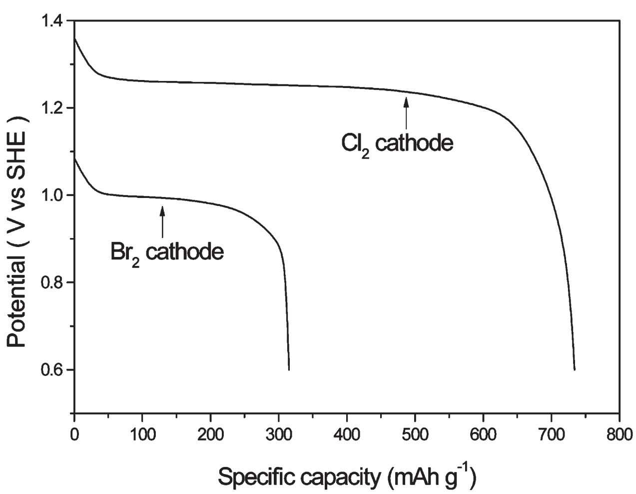

Fig. 2 Capacity discharge curves of the alkaline Cl_2 and Br_2 cathodes at constant current density of 1 mA cm^{-2}.

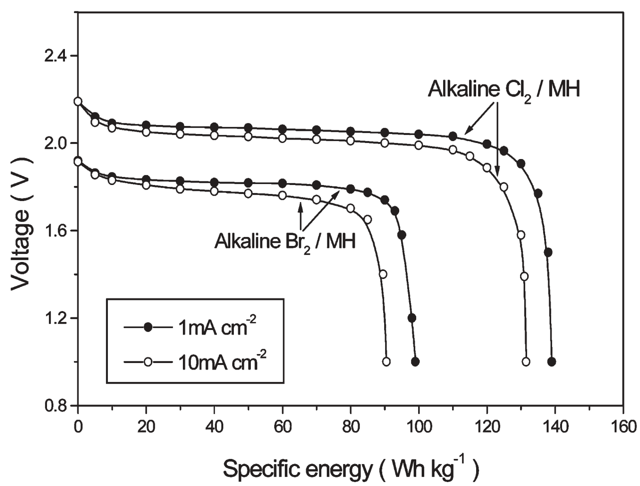

Fig. 3 Energy capacity curves of alkaline halogen batteries. The anode was 60 mA h MH, the anolyte was 10 M KOH, the catholyte was 0.2 M KCl and 0.2 M KBr respectively. Cells were discharged to 1.0 V at current density of 1 mA cm^{-2} and 10 mA cm^{-2}.

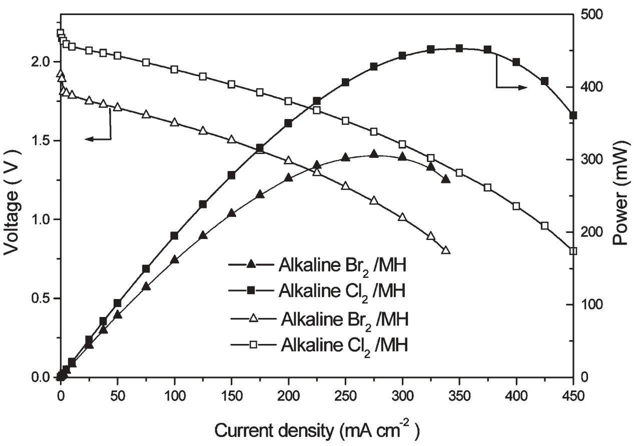

Fig. 4 Discharge properties of alkaline halogen batteries at 298 K.

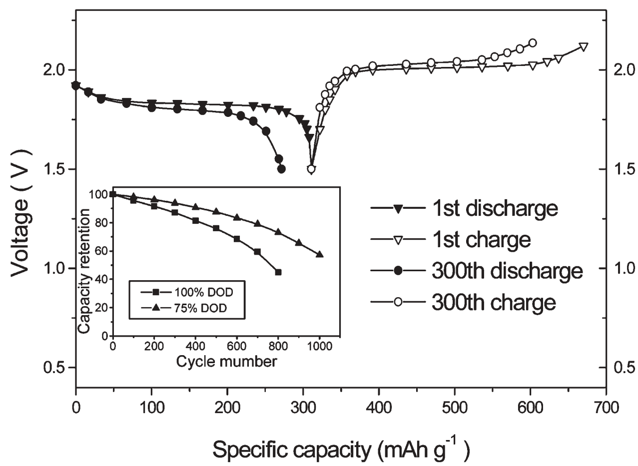

Fig. 5 Charge–discharge performance of alkaline halogen batteries recorded at lower current density of 1 mA cm^{-2}.

Evidence for the RAH batteries is provided by discharge properties of alkaline Br_2/MH and alkaline Cl_2/MH batteries at 298 K. The power of alkaline halogen batteries was measured with variational discharge current level. The discharge current was adjusted from weak to strong, until the discharge potential fell to 0.8 V. The results suggest that the alkaline halogen battery has higher power density than the conventional Ni/MH battery. The resulting peak power density reached 236 mW cm^{-2}, 92% higher than that of 122 mW cm^{-2} for the conventional Ni/MH cell. The alkaline Cl_2/MH cell has much higher output power density of 315 mW cm^{-2} due to its higher discharge voltage. Alkaline halogen battery has a very high power density due to three factors. First, the discharge voltage of the alkaline halogen battery is higher than that of the conventional Ni/MH battery. Secondly, the electrolyte of the alkaline halogen battery is KOH (or NaOH) and KBr (or KCl) solution, which significantly reduces the internal resistance of the cell. And finally, the halogen cathode has high activity and low polarization. In future experiments, further increase in energy capacity and power density will be expected with optimization for the alkaline halogen batteries.

We studied the reversibility and energy efficiency of RAH batteries with bromine cathode and the alkaline MH anode during repeated charge-discharge cycling. Fig. 5 presents the typical charge-discharge behavior of these batteries. From the experiment results, we can see that alkaline halogen battery is significantly rechargeable. The alkaline Br_2/MH cell can be discharged for 500 cycles at 100% depth of discharge (DOD) and more than 800 cycles at 75% DOD. The charge and discharge curves of alkaline Br_2/MH cell are very flat. The experiment also provides the evidence that alkaline halogen battery has higher energy efficiency of charge and discharge. Charging and discharging at current density of 1 mA cm^{-2}, the energy efficiency for the alkaline MH/Br_2 cell is 83% compared to that of Ni/MH is 66%. The discharge capacity and voltage of RAH batteries decay during 300 cycles of charge and discharge (Fig. 5) because the MH electrode itself has attenuation rate and the property of DSA electrode is decreased in a certain extent during the redox of halogen. That leads to the decrease of discharge voltage of cells.

We have demonstrated that RAH batteries have greater energy capacity and power density than the existing nickel system such as alkaline Ni/MH batteries. Further research of stability and storage of other relevant halogen cathodes in alkaline electrolyte and more superior cation exchange membrane will be needed. For example, halogen cathodes containing halogen inter-compounds such as $BrCl_5$ or ICl_7, and halogenoids such as $(SCN)_2$ and $(OCN)_2$, also exhibit their superiority in high potential, capacity and reaction activity. We expect that further improvements in these batteries will make them a viable alternative to current rechargeable alkaline batteries.

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Notes and references

1 Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa and T. Miyasaka, *Science*, 1997, **276**, 1395–1397.
2 (*a*) S. Licht, B. H. Wang and S. Ghosh, *Science*, 1999, **285**, 1039–1042; (*b*) J. Kim and A. Manthiram, *Nature*, 1997, **390**, 265–267.
3 (*a*) F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature*, 1998, **394**, 456–458; (*b*) S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merle, *Nature*, 2001, **410**, 910–913.
4 T. Ise, T. Hamamatsu, T. Imoto, M. Nogami and S. Nakahori, *J. Power Sources*, 2001, **92**, 81–87.
5 S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 2002, **1**, 123–128.
6 L. Eriksson, U. Palmqvist, H. Rundlöf, U. Thuresson and R. Sjövall, *J. Power Sources*, 2002, **107**, 34–41.
7 R. M. Dell, *Solid State Ionics*, 2000, **134**, 139–158.
8 S. Jouanneau, A. Le Gal LaSalle and D. Guyomard, *Electrochim. Acta*, 2002, **48**, 11–20.

