ELSEVIER

Journal of Power Sources 54 (1995) 151–154

JOURNAL OF POWER SOURCES

Practical batteries based on the SWING system

Klaus Brandt

VARTA Batterie AG, Research and Development Centre, Gundelhardtstrasse 72, 65779 Kelkheim, Germany

Abstract

In order to find a wide range of applications using a new cell chemistry, many different factors such as cell voltage, energy density, power density, safety, reliability, life, cost and environmental impact have to be considered. The lithium-ion or SWING system demonstrated a specific energy of more than 100 Wh/kg in small cells and more than 80 Wh/kg in large cells with an approximately 100 Wh energy content, and a cycle life of more than 1000 cycles in cells with $LiCoO_2$ cathodes. When a manganese oxide-based cathode was used it has furthermore the potential to become a low cost system without the use of heavy metals.

Keywords: Rechargeable lithium batteries; Lithium-ion batteries; Cathodes; Manganese dioxide

1. Introduction

For more than twenty years, the promise of high energy density has motivated researchers and companies to develop rechargeable lithium batteries. A large number of electrochemical systems has been evaluated, some of which are now being used in small button cells produced by a number of Japanese companies [1]. Efforts to introduce spirally-wound cylindrical cells based on systems such as lithium metal/MoS_2 [2] and lithium metal/MnO_2 [3,4] into the market were short lived, mostly due to safety problems. Now, a system based on a lithium–carbon intercalation compound anode, a lithiated cobalt oxide cathode ($Li_xC_6/Li_{1-x}CoO_2$), and a liquid organic electrode is being manufactured by Sony Corporation [5] and used to power cellular telephones, video camcorders and note book computers. A number of other companies have announced their intention to manufacture similar systems. Despite this apparent success of the lithium-ion, or rocking-chair cells or SWING system, as it is also called, other systems, especially polymer electrolyte systems and lithium metal anode systems, are persued in parallel by various organizations.

It is believed that the field of applications for rechargeable lithium batteries will initially be a portable equipment such as cellular telephones, portable computers and some high-end consumer devices, for example video- and camcorders [6]. The prospects of using large lithium batteries for powering electric vehicles (EV) are also investigated by the US Advanced Battery Consortium (USABC) [7], the Japanese Lithium Battery Energy Storage Technology Research Association (LiBES) [8] and through European Union sponsored programs.

In order to evaluate the probability of success of such a battery system in these applications, its energy density, cell voltage, power density, safety and reliability, life, cost and environmental impact have to be considered.

2. SWING system evaluation

2.1. Cell voltage

The portable electronic equipment has typical operating voltages between 3 and 12 V. For some equipment which has now operating voltages above 3 V such as cellular telephones, there is a trend to lower the operating voltages to 3 V. A battery based on Ni/Cd or Ni/MeH chemistry requires three cells connected in series for such an application. A SWING system with a graphite-based anode and a $LiCoO_2$ cathode or a $LiMn_2O_4$ cathode delivers all its capacity above 3 V and its single-cell voltage characteristics closely matches that of three Ni/MeH cells in series (Fig. 1). This compatibility of the voltage characteristics can increase the speed of replacement of the Ni/Cd and Mi/MeH technologies with the SWING technology in portable equipment applications. Saving two cell cases and associated hardware reduces cost and increases energy density.

SSDI 0378-7753(94)02058-B

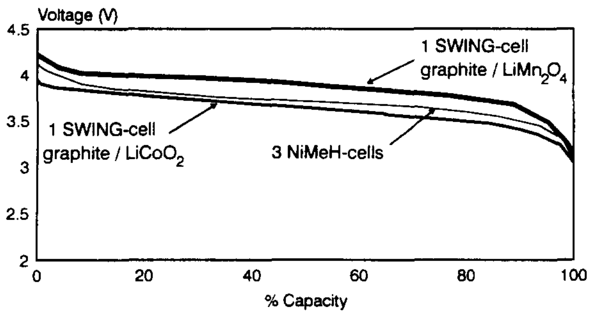

Fig. 1. Comparison of the voltage profiles of one SWING cell with three Ni/MeH cells connected in series. Both cells with $LiCoO_2$ and $LiMn_2O_4$ cathode are shown. Discharge rate is 0.2*C*.

For large batteries, for example EVs, a higher cell voltage is also of an advantage as it reduces the number of cells required to achieve the battery voltage. A smaller number of cells reduces the complexity of the battery and the battery management system.

2.2. Energy density

At first look, replacing lithium metal with a carbon intercalation system as the anode will reduce the system's energy density. However, the loss of lithium metal during cycling requires a large lithium excess anode [9], and the useful capacity per weight and per volume is typically reduced by a factor 4. Therefore, the weight penalty for SWING with a graphite anode is quite small. In volume terms, there is no penalty at all (Table 1). The theoretical specific energy of SWING systems is comparable with most lithium metal anode systems and about twice as high as that of alkaline rechargeable systems (Table 2). In small laboratory cells, more than 100 Wh/kg and 240 Wh/l have been demonstrated [10]. Commercially available cells of sizes ranging from 1 to 10 Wh per cell have only slightly lower values.

The scale-up of cell sizes for use in large batteries at VARTA has begun recently using both graphite/ $LiCoO_2$ and the graphite/$LiMn_2O_4$ chemistry. Prismatic cells with an energy content from 40 Wh to more than 100 Wh have been developed by VARTA.

Fig. 2 shows the Ragone diagram for two types of cell with a manganese oxide-based chemistry. The first cell developed, Mark 1, has an energy content of 42 Wh and a specific energy of 51 Wh/kg at a 10 h (0.1 *C*) rate. The larger cell, Mark 2, shows a significant increase to 103 Wh and 86 Wh/kg.

This is a significant advantage in energy density compared with other room temperature battery systems which are also being considered for the EV application such as lead/acid with 30 Wh/kg and Ni/MeH with 65 Wh/kg [11].

2.3. Power density

Organic electrolytes used in lithium batteries have a conductivity between 10^{-3} and 10^{-2} S cm^{-1} [11], i.e., about two orders of magnitude below typical aqueous electrolytes. The low conductivity will limit the rate capability of organic electrolyte cells. This is in part compensated by using very thin electrodes in SWING cells. The present limit to rate capability of small cells is about 2*C* during continuous discharge at room temperature [12]. This is, however, sufficient for the applications under discussion. Most portable equipment demands a continuous rate capability of 1*C* or less.

Large cells do not have the same high rate capability at present. Fig. 2 shows a significant drop in energy when the continuous discharge rate exceeds 0.5*C*. As can be seen by comparing the Ragone curves for Mark 1 cells at two different temperatures, the rate-limiting mechanism is thermally activated. The lower rate capability of these cells is due to the use of thicker electrodes. Continuous power is limited by mass transport in the electrolyte.

2.4. Safety and reliability

As mentioned in Section 1, early efforts to commercialize lithium batteries failed because of safety problems. These were caused by a change in the morphology of the lithium metal anode, e.g., a highly porous dendritic deposit which can undergo strong exothermic reactions with the electrolyte at elevated temperatures [13]. Heating of the cell that leads to violent reactions cannot only occur through external sources but also through abuse such as short circuit or high rate overcharge. The use of a carbon intercalation compound in the SWING system avoids the change in morphology of the anode during cycling and is therefore intrinsically safer. Some safety concern exists in cells with a $LiCoO_2$

Table 1
Theoretical capacity of various anode materials per weight and per volume. Li * includes a fourfold excess of lithium for sufficient cycle life.

Anode material	Useful range of Δx	Capacity per weight (mAh/g)	Capacity per volume (mAh/cm^3)
$(1-x)$Li (metal)	1	3861	2062
$(1-x)$Li * (metal)	0.25	965	515
Li_xC_6 (coke)	0.5	186	372
Li_xC_6 (graphite)	1.0	372	837

Table 2
Theoretical specific energy for various lithium battery systems. For Li *, a fourfold lithium excess is assumed. NiCd for comparison. (g) = graphite.

System	Assumed reaction	Average voltage (V)	Specific energy (Wh/kg)
Li *$/TiS_2$	$Li + TiS_2 \leftrightarrow LiTiS_2$	2.1	403
Li *$/MoS_2$	$0.8Li + Li_{0.2}MoS_2 \leftrightarrow LiMoS_2$	1.8	212
Li *$/V_2O_5$	$Li + V_2O_5 \leftrightarrow LiV_2O_5$	3.1	396
C_6(g)$/LiCoO_2$	$0.5LiC_6 + Li_{0.5}CoO_2 \leftrightarrow 0.5C_6 + LiCoO_2$	3.6	360
C_6(g)$/LiNiO_2$	$0.7LiC_6 + Li_{0.3}NiO_2 \leftrightarrow 0.7C_6 + LiNiO_2$	3.5	444
C_6(g)$/LiMn_2O_4$	$LiC_6 + Mn_2O_4 \leftrightarrow C_6 + LiMn_2O_4$	3.8	403
Ni/Cd	$2NiOOH + 2H_2O + Cd \leftrightarrow 2Ni(OH)_2 + Cd(OH)_2$	1.2	210

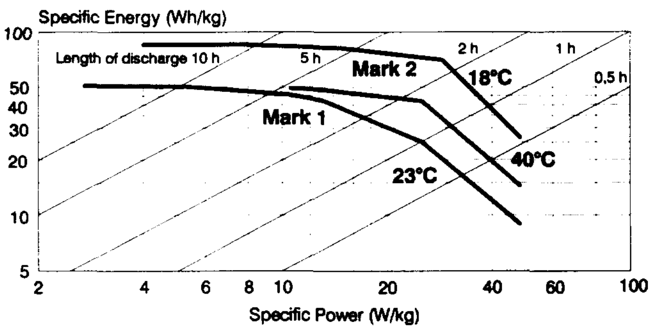

Fig. 2. Ragone plot (specific energy vs. specific power) for two sizes of prismatic cells with $LiMn_2O_4$ cathode. Cell size: Mark 1, 42 Wh; Mark 2, 103 Wh. Mark 1 data are given for a temperature of 23 and 40 °C.

cathode. There is excess lithium in the cathode (Table 2) which can be plated during overcharge. Special safety mechanisms applicated in the cell [14] or individual cell voltage control [15] have been employed to avoid this risk.

Reliability of lithium metal anode cells was limited by internal short circuits caused by lithium dendrites penetrating the separator after hundred cycles [16]. Under normal operating conditions, lithium will not be plated in SWING cells, removing one of the main failure mechanisms.

The effect of the voltage of a single cell on the reliability of a battery has to be considered. As discussed above, many portable applications will require only one SWING cell. This greatly improves the reliability in comparison with multicell Ni/Cd batteries, which require cell capacity matching to avoid early failure.

2.5. Life

The cycle-life requirements are 300 to 500 cycles for portable equipments, ≥1000 cycles for EV applications. Lithium metal anode cells do not meet these requirements [9], even those that employ polymer electrolytes [17]. SWING systems, on the other hand, have demonstrated more than 1000 charge/discharge cycles in small cells with a $LiCoO_2$ cathode.

A negative aspect of the SWING system is its sensitivity to storage at elevated temperature. Storing cells at temperatures above 45 °C leads not only to an increased rate of self-discharge but also to a permanent reduction in cell capacity [18].

Less experience exists with the cycle life of large cells and cells with a $LiMn_2O_4$ cathode. Fig. 3 shows the present status of the cycle-life tests of a Mark 1 cell with a $LiMn_2O_4$ cathode and a Mark 2 cell with a $LiCoO_2$ cathode. So far, more than 100 cycles have been achieved with the Mark 1 cell. The tests are being continued.

2.6. Cost

Cost is one of the most important aspects of practical batteries. For small rechargeable batteries, the benchmark is the Ni/Cd system, for large batteries it is the lead/acid system. The SWING system can use low-cost graphite materials for the anode, thus the cost of active materials is dominated by the choice of the cathode material. Table 3 gives the cost of the metal in the cathodes of a 1 kWh Ni/Cd, and the SWING battery with either a $Li_{1-x}CoO_2$ ($1 \le x \le 0.5$), or $Li_{1-x}NiO_2$ ($1 \le x \le 0.5$) or $Li_{1-x}Mn_2O_4$ ($1 \le x \le 0$) cathode.

Comparing these figures with the USABC target of a selling price of US $ 100/kWh for the complete EV battery shows clearly that manganese oxide is the cathode material of choice. Today, the SWING technology

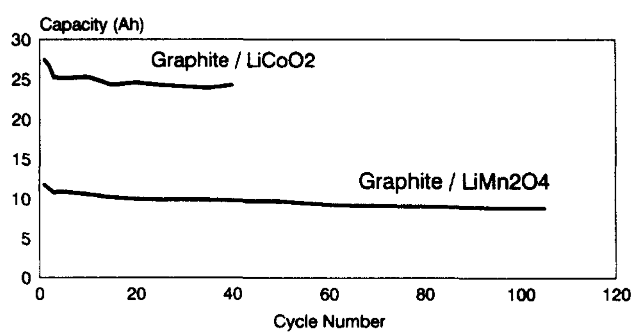

Fig. 3. Cycle-life plot for a prismatic cell of Mark 1 with $LiMn_2O_4$ cathode and a Mark 2 with $LiCoO_2$ cathode. Discharge rate is 0.33*C*.

Table 3
Cost of the metal content of the cathode for various SWING systems. Ni/Cd for comparison.

System	Cathode	Kg of metal/ kWh [a]	Metal cost [b] ($/kg)	Metal cost ($/kWh)
Ni/Cd	NiOOH	1.83	6.10	11.20
SWING	$LiCoO_2$	1.22	48.50	59.20
	$LiNiO_2$	1.22	6.10	7.40
	$LiMn_2O_4$	1.08	3.00	3.24

[a] Assumes a one-electron reaction for NiOOH, and a reaction of 0.5 electrons per metal atom for the SWING cathodes.
[b] Average metal prices at the London Exchange, 1 Feb. 1994.

has not been developed sufficiently to give reliable estimates for mass-produced batteries. However, it is expected that its selling price per Wh will eventually be below that of Ni/Cd.

2.7. Environmental impact

The impact on the environment of some of the metals is of a major concern, especially when heavy metals are used. For established battery technologies, recycling is a solution. For lead/acid batteries, efficient recycling is in place. For Ni/Cd, some recycling efforts do exist, however costs are high. A SWING system with a carbon anode and a lithium manganese oxide cathode requires new recycling methods, but would avoid the heavy metal problem.

3. Conclusions

It has been shown that the SWING system performs well when it is evaluated on six criteria: energy density; cell voltage; power density; safety and reliability, and cost and environmental impact. It becomes also evident that to a system using a manganese oxide cathode would be given preference, based on the two criteria of cost and environmental impact.

The weaknesses of the system, at its present stage of development, are the requirement for individual cell voltage control, loss of capacity after high temperature storage, and the lack of fast charge capability.

The author believes that significant improvement in specific energy in excess of 150 Wh/kg and high temperature stability are to be expected in the future. High performance combined with potential of low cost per energy will ensure the success of the SWING system in portable equipment applications.

For the same reasons, the SWING system is also a serious candidate for EV batteries. Here, the use of polymer electrolytes is being considered. These electrolytes will make bipolar constructions feasible and thus further increase the specific energy bringing the SWING system close to the long-term targets of the USABC.

References

[1] Z. Takehara, *J. Power Sources, 26* (1989) 257.
[2] F.C. Laman, in C.D.S. Tuck (ed.), *Modern Battery Technology*, Ellis Horwood, New York, 1991.
[3] K. Brandt and M. Juzkow, *Proc. 5th Int. Meet. Lithium Batteries, Beijing, China, 27 May–1 June 1990.*
[4] Sony's lithium-manganese rechargeable battery, *JEC Battery Newslett.* (Feb.) (1988) 26.
[5] T. Nagaura, *Proc. 5th Int. Seminar on Lithium Battery Technology and Applications, Deerfield Beach, FL, USA, 5–7 Mar. 1990.*
[6] Sony Corporation Battery Group and Sony Energytec, *JEC Battery Newslett., (July–Aug.) (1993)* 19.
[7] *Advanced Battery Technol., 28* (Dec.) (1992) 1.
[8] *Advanced Battery Technol., 29* (July) 1993) 6.
[9] F.C. Laman and K. Brandt, *J. Power Sources, 24* (1988) 195.
[10] J. Yamaura, Y. Ozaki, A. Morita and A. Ohta, *J. Power Sources, 43/44* (1993) 233.
[11] F.J. Kruger, K. Brandt and U. Köhler, *Proc. 11th Int. Seminar Primary and Secondary Battery Technology and Application, Deerfield Beach, FL, USA, 28 Febr.–4 Mar. 1994.*
[12] J.T. Dudley *et al. J. Power Sources, 35* (1991) 59.
[13] D.P. Wilkinson, J. Dahn, U. von Sacken, *Ext. Abstr., Fall Meet. The Electrochemical Society, Seattle, WA, USA, 14–19 Oct. 1990.*
[14] S. Oishi, T. Abe and T. Nagaura, *US Patent No. 4 943 497* (1990).
[15] Y. Eguchi, M. Sato, T. Narashima and A. Sanpei, *Eur. Patent Applic. 0 525 744A1* (1992).
[16] K. Brandt and F.C. Laman, *J. Power Sources, 25* (1989) 265.
[17] R.J. Brodd, J.T. Lundquist, J.C. Morris and D.R. Shackle, *Proc. 9th Annual Battery Conf. Applications and Advances, Long Beach, CA, USA, 10–12 Jan. 1994.*
[18] R. Herr and J. Kümpers, *Ext. Abstr., Fall Meet. The Electrochemical Society, Miami Beach, FL, USA, 9–14 Oct. 1994.*