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Recent progress in rechargeable nickel/metal hydride and lithium-ion miniature rechargeable batteries

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Abstract

VARTA is searching for alternative battery solutions for memory back-up and bridging applications, and for this, it is developing nickel/metal hydride and lithium-ion button cells. Presented are the results on different sizes and forms of lithium-ion cells (621, 1216 and 2025) containing different electrode materials and shapes. Presently, the most favoured cathode material is lithiated manganese dioxide. The electrodes are made from both solid and porous materials and, together with an organic electrolyte, result in a cell system with a voltage level of approximately three. Included are results, both from these lithium-ion cells, and also from ones using the nickel/metal hydride system.

Keywords: Applications/electronic equipment; Nickel/metal hydride rechargeable batteries; Lithium-ion rechargeable batteries; Lithiated transition metal oxides

1. Introduction

Committed to the development and introduction of new electrochemical systems to be used in button cells for memory backup applications (MBU), VARTA has, in recent years, switched totally from nickel/cadmium to the nickel/metal hydride system for MBU and bridging applications. These cells are nowadays used in many PC and notebook computers. VARTA is searching for alternative battery solutions for these applications and therefore, is developing high rate, high capacity, new generation nickel/metal hydride and lithium-ion button cells. In this paper, we look at different sizes (V400HR, IC 621, MC 2025) with different electrode materials and different shapes of electrodes. Accordingly, for this we concentrated on new metal hydride electrode technologies and also on the use of a new, highly stable, lithiated manganese oxides in our lithium-ion button cells.

Many rechargeable lithium systems are well-known and used in button cells. But none of them meets all of the required criteria. Our new products meet all the criteria and combine novel, low cost, environmentally friendly, lithiated, manganese dioxide cathodes with graphitized carbon anodes.

Details of the electrochemical results on high rate nickel/metal hydride button cells and on very stable materials for rechargeable lithium-ion button cells are given.

2. Applications for rechargeable miniature batteries

The applications to which various types of presently available batteries are suited may be summarised as:

(a) Li-ion, button	Cellular telecom, pager, data processing
(b) Li: flat, prismatic/polymer	Smart cards, data processing, telecom, consumer
(c) Ni/metal hydride, high temp. button	Domestic, timers, special MBU
(d) Ni/metal hydride, button	MBU, CP, industrial, medical, automotive
(e) Ni/metal hydride, high rate button	Digital CP, bridging, DRAM MBU, two-way pager, scanner

Some of the key requirements for MBU and bridging applications include:

(a) Only 10% of available capacity is used,

(b) Modern electronic devices require reduced power and voltage,

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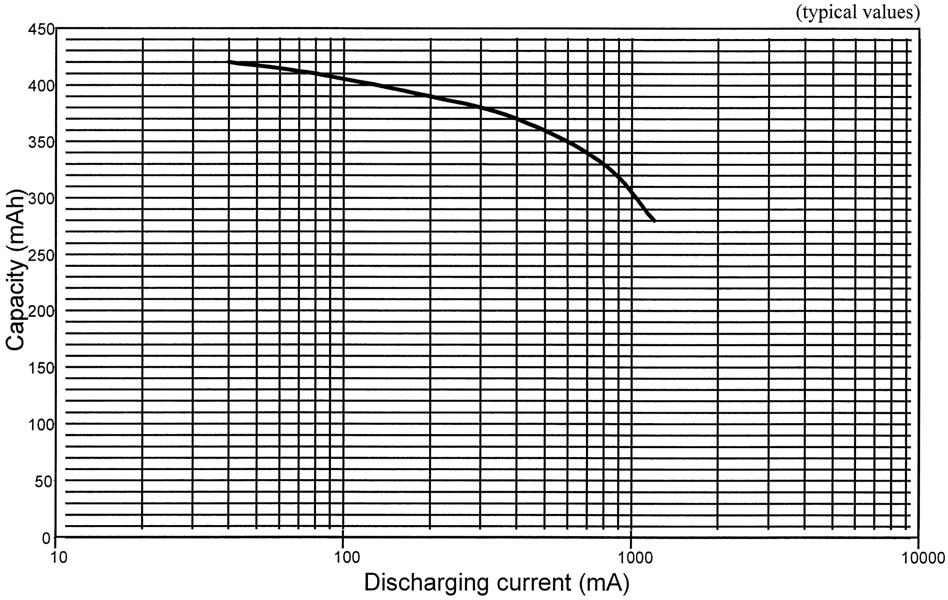

Fig. 1. Room temperature capacities of the V400HR cell when discharged at currents between 40 and 1000 mA.

(c) A wide operating temperature range, typically −20 to +70°C,
(d) Stable on deep discharge to 0 V,
(e) Short circuit stability,
(f) Long cycle life,
(g) Environmentally friendly components,
(h) Low cost.

3. High rate nickel / metal hydride V400HR cell

This 4.7-mm thick button cell has a nominal capacity of 400 mAh and even when discharged at the 2.5 C rate, gives 300 mAh (Fig. 1). Cycling capability is excellent. Fig. 2 shows a drop in capacity of only a few percent over 500 cycles of 200 mA charge for 2.4 h, 200 mA discharge to 2 V. The high rate capability is achieved by using a highly porous foam for the electrodes.

Additional characteristics of this cell include:
(a) A sealed cell with a pressure relief vent,
(b) A 4- to 6-year battery life,
(c) Permanent fixing in the application: a cost-saving feature,
(d) Good performance on trickle charge,
(e) Competitively priced, compared to other types of nickel / metal hydride cells,

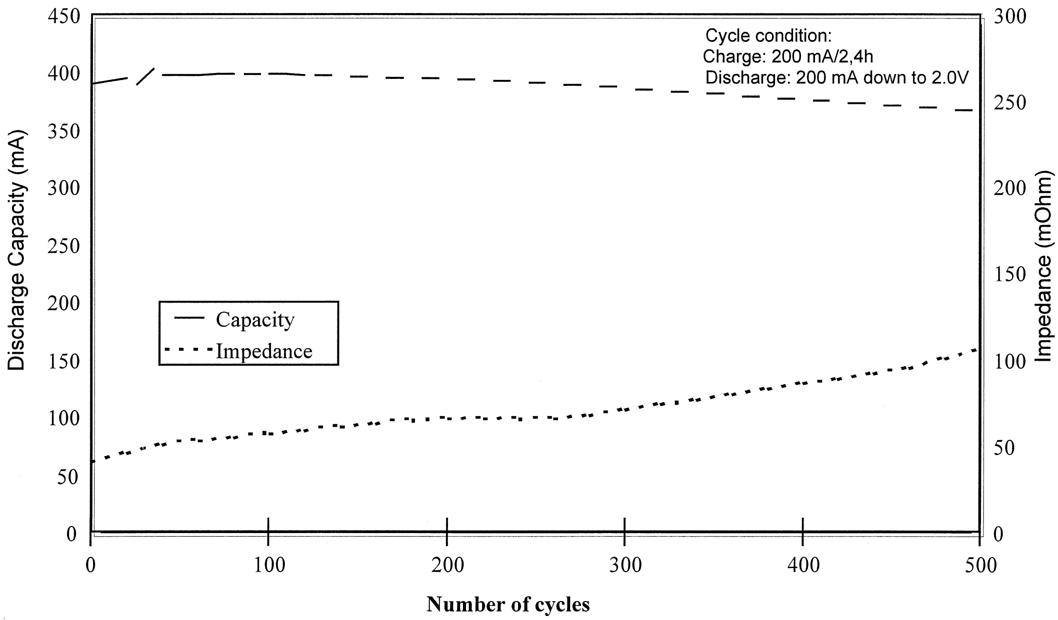

Fig. 2. V400HR cell. Variation in capacity and impedance over 500 cycles. Charge: 200 mA for 2 h. Discharge: 200 mA to 2.0 V.

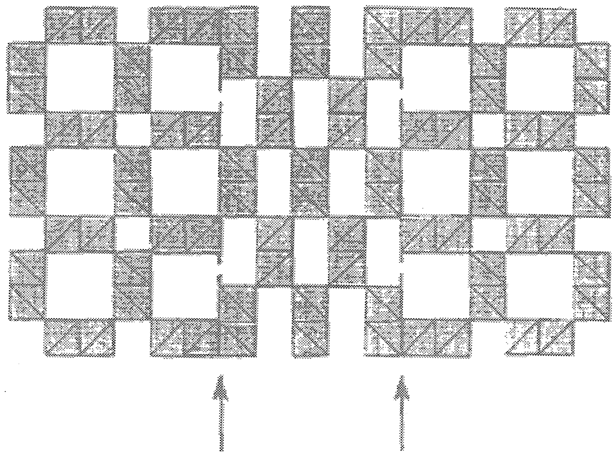

Fig. 3. Structure of Ramsdellite α-manganese dioxide.

(f) No safety devices needed for one- or two-cell batteries,
(g) UL recognition pending,
(h) A 1-h fast-charge capability.

4. α-Manganese oxides for use in lithium-ion button cells

Four lithiated α-manganese dioxides have been characterized. X-ray diffraction patterns show that either a $Li_2O \cdot MnO_2$ phase (sample A, B and C) or a Ramsdellite–MnO_2 phase (sample D) stabilizes the $\alpha LiMnO_2$ structure and provides good rechargeability. The presence of several percent of Li_2MnO_3 is necessary.

The composition of the four samples was:
Sample A—$Li_{0.42}MnO_2$
Sample B—$Li_{0.50}MnO_2$
Sample C—$Li_{0.35}MnO_2$
Sample D—$Li_{0.33}MnO_2$.

The structure of sample D, the Ramsdellite α-MnO_2, is shown in Fig. 3. Thermogravimetric analysis has shown a relationship between the cycling behaviour and the water content within the large [2*2] channels of the α-MnO_2 structure and verifying the theory. With the Li_2O . . . MnO_2-stabilized (samples A–C) the water molecules can be replaced by Li_2O. The different α-Li_x, MnO_2 samples each deliver a better cycling performance with decreasing water content. Table 1 shows the specific discharge capacities of the various lithiated manganese oxides and Fig. 4 shows discharge and cycling performances.

An example of a commonly available product in which we have tested these new cathode materials is our MC621 battery, 2.1 mm thick × 6.8 mm diameter (Fig. 5). With this lithium-ion cell we achieved more than 200 cycles at 100% DOD, more than 1000 cycles at 10% DOD at a cell capacity of 1.1 mAh.

Fig. 4 is a comparison of the performance of these four oxides when cycled between 3.4 and 1.8 V at a current density of 0.2 mA cm^{-2}. The superior cycling ability of

Table 1
Specific discharge capacities

	Stoichiometry	Intercalated lithium (mol)	Discharge capacity (mAh g^{-1})
Sample A	$Li_{0.42}MnO_2$	0.52	154
Sample B[a]	$Li_{0.50}MnO_2$	0.53	156
Sample C	$Li_{0.35}MnO_2$	0.56	162
Sample D	$Li_{0.33}MnO_2$	0.59	180

[a] Sample B is a new material.

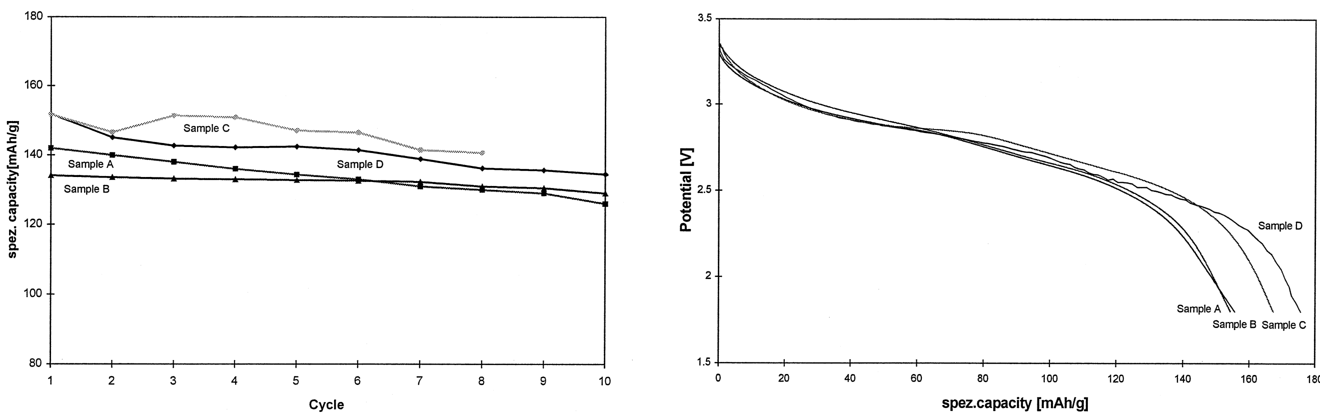

Fig. 4. Cycling and discharge performances of the four samples of lithiated manganese dioxide. Electrolyte: $LiPF_6$ in EC/DMC. Cycled between 3.4 and 1.8 V at 0.2 mA cm^{-2}.

Key characteristics of MC621

	Cell Size [mm]	Cathode	Anode	operation voltage [V]	Nom. capacity [mAh]	Cycle life [10% DOD]	Cycle life [100% DOD]	Storage [10d @60C]
Spec.	6.8 x 2.1	Li_xMnO_2	Li_xC_6 graphite	0 - 3.3	1.1	> 1000	> 200	< 10% irrev. loss

UL number: 13654 (pending)

Fig. 5. Characteristics of the MC621 lithium-ion button cell.

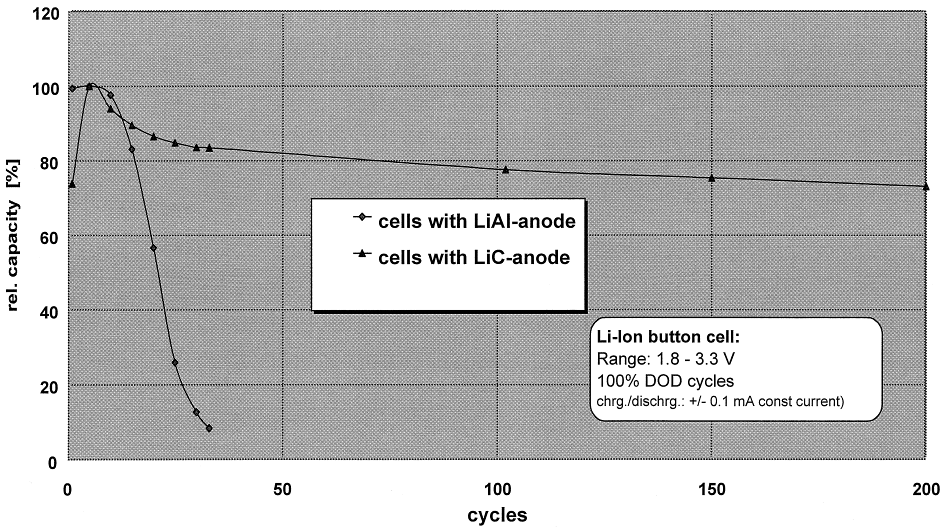

Fig. 6. Cycling behaviour of the lithiated manganese dioxide (sample C) against lithium carbon (LiC) and lithium alloy (LiAl) anodes.

using lithium-ion anode (LiC) over a lithium–alloy variant (LiAl) is shown in Fig. 6.

5. Characteristics of the lithium-ion button cell

In summary:

(a) The carbon intercalating cathode gives excellent cycle life,

(b) With no metallic lithium present, there is no safety risk,

(c) Not sensitive to deep discharge,

(d) Operates over temperature range −10 to +60°C,

(e) No self-discharge,

(f) Excellent charge retention in charged or discharged state,

(g) Contains only environmentally friendly materials,

(h) UL recognition pending (number 13654).