

# Safety characteristics of rechargeable lithium metal cells

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## Abstract

We have developed a prototype AA-size cell which consists of an amorphous  $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$  (95:5 in molar ratio) cathode, a lithium metal anode and an organic electrolyte (Li/ $a\text{-V}_2\text{O}_5$  cell). Preliminary safety tests including electrical, thermal and mechanical abuse tests and cell performance tests were carried out on this Li/ $a\text{-V}_2\text{O}_5$  cell. Based on these experimental results, we discuss the safety characteristics and the future prospects for rechargeable lithium metal cells. © 1997 Elsevier Science S.A.

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## 1. Introduction

The rapid progress in the field of portable electronic equipment has made it necessary to develop new higher energy density cells. A rechargeable cell with a lithium metal (Li) anode is attractive because, theoretically, it has a higher energy density than a lithium-ion battery. However, cylindrical rechargeable lithium metal cells are not commercially available today. One of the most important factors determining whether or not rechargeable lithium metal cells become commercially available is cell safety. Cell safety is affected by many factors and there is currently insufficient information about the safety of practical lithium metal cells.

We have developed a prototype AA-size cell which consists of an amorphous  $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$  (95:5 in molar ratio) cathode, a lithium anode and an organic electrolyte (Li/ $a\text{-V}_2\text{O}_5$  cell) [1]. In this report, we discuss the safety characteristics of lithium metal cells based on the results of experiments we performed on this Li/ $a\text{-V}_2\text{O}_5$  cell to determine its resistance to electrical, thermal and mechanical abuse. The electrical abuse tests we undertook consisted of external short, overcharge and forced discharge tests. The thermal abuse tests consisted of heating the cell at various temperatures. The mechanical abuse tests comprised nail penetration and crushing both with a bar and a flat plate.

## 2. Experimental

### 2.1. Preparation of $a\text{-V}_2\text{O}_5$

$a\text{-V}_2\text{O}_5$  was used as the cathode active material. In order to obtain  $\text{V}_2\text{O}_5$  in an amorphous state easily, we mixed it with

a small amount of  $\text{P}_2\text{O}_5$ .  $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$  (95 mol%  $\text{V}_2\text{O}_5$ ) was prepared by melting reagent-grade raw oxides in platinum crucibles for 1 h at 750 °C, followed by quenching on a water-cooled iron block [3].

### 2.2. Fabrication of the AA-cell

An  $a\text{-V}_2\text{O}_5$  cathode, comprising  $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ , carbon and polymer binder, was coated and pressed on a sheet of aluminum foil by the conventional slurry coating method. LiAsF<sub>6</sub>/ethylene carbonate-based mixed electrolyte was used because of its high lithium cycling efficiency as well as its high lithium-ion conductivity [4]. The AA-cell we fabricated has a pressure vent, a Polyswitch™ (PS; Raychem, thermal and current fuse) and is composed of a spirally wound cathode sheet, a metallic Li-based anode sheet and a polyethylene (PE) separator [1,2]. Charge/discharge cycling tests were performed galvanostatically at 21 °C in standard charge/discharge voltage range of between 1.5 and 3.3 V.

## 3. Results and discussion

### 3.1. Performance of the Li/ $a\text{-V}_2\text{O}_5$ cell

The performance of our AA-size prototype Li/ $a\text{-V}_2\text{O}_5$  cell is shown in Table 1. Fig. 1 shows its discharge curves. The Li/ $a\text{-V}_2\text{O}_5$  cell has an energy of 2 Wh (900 mAh), energy densities of 110 Wh/kg and of 250 Wh/l, and a cycle life of 150–300 cycles depending on the discharge and charge cur-

Table 1  
Characteristics of an AA-size Li/a-V<sub>2</sub>O<sub>5</sub> cell

Cell characteristics	Values
Volume, weight	8 cm <sup>3</sup> , 18 g
Voltage range	3.3–1.4 V
Current range	discharge: 400–2000 mA, charge 100–200 mA
Nominal capacity	900 mAh (2 Wh)
Energy density	110 Wh/kg, 250 Wh/l
Cycle life	150–300 cycles
Self-discharge rate	1% per month at 21 °C

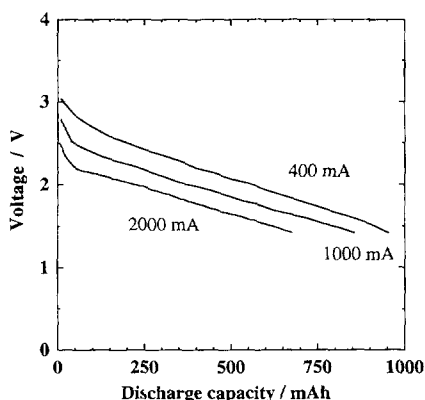


Fig. 1. Discharge curves of AA-size Li/a-V<sub>2</sub>O<sub>5</sub> cells at 21 °C

rents [1,2]. A discharge current of more than 400 mA should be used for practical applications from the viewpoint of cycle life and cell safety [1,2]. This is because the cycle life and thermal stability of a rechargeable lithium metal cell is reduced by the exfoliation of deposited lithium from the anode at lower discharge current [5,6]. The recommended charge current is less than 200 mA because larger charge

Table 2  
Safety test results for AA-size Li/a-V<sub>2</sub>O<sub>5</sub> cells<sup>a</sup>

Abuse test	Test conditions	Fresh cell	Results (○: no fire)			
			Discharge current: 1000 mA		Discharge current: 400 mA	
			Cycled 75 times	Cycled 150 times	Cycled 60 times	Cycled 120 times
External short	Room temperature	○	○	○	○	○
	40 °C	○	○	○	○	○
Forced discharge <sup>b</sup>	Room temperature	○	○	○	○	○
	40 °C	○	○	○	○	○
Overcharge	Charge	Room temperature	○	○	○	○
	200 mA		40 °C	○	○	○
	Charge	Room temperature	○	○	○	○
	600 mA		40 °C	○	○	○
Crush	Room temperature round bar	○	○	○	○	
	Room temperature, flat plate	○	○	○	○	
Nail penetration	Room temperature	○	○	○	○	
Thermal stability (maximum safe temperature)	5 °C/min Held at a given temperature	130 °C	150 °C	150 °C	140 °C	130 °C

<sup>a</sup> Precycling conditions: charge current = 200 mA; discharge current shown in the Table, and cycling number shown in the Table

<sup>b</sup> Forced discharge: short test of four-cell pack connected in series. Three cells are in a fully charged state, and one cell is discharged to 1.5 V.

current leads to a reduction in cycle life. This is caused by the deposition of dendrite lithium as a result of the inability of organic electrolyte with low conductivity to supply sufficient lithium cations.

### 3.2. Safety of the Li/a-V<sub>2</sub>O<sub>5</sub> cell

The results of safety tests are summarized in Table 2. The cells we tested were fully charged to 3.3 V unless otherwise noted. A fresh cell in Table 2 is a pretreated Li/a-V<sub>2</sub>O<sub>5</sub> cell after cell fabrication. The pretreatment is done by cycling the cell twice with a 600 mA discharge and a 200 mA charge between 1.5 and 3.3 V. The results of the external short, overcharge, forced discharge, nail penetration, crush and heating tests, are described briefly below.

#### 3.2.1. External short

Fig. 2 shows the results of external short circuit tests on the AA Li/a-V<sub>2</sub>O<sub>5</sub> cell. The tests were carried out through 30 mΩ resistance. We experienced no safety problems during these tests because of the presence of the Polyswitch inside the cell. We confirmed that even if the Polyswitch fails to operate, the short-circuit current stops flowing before thermal runaway occurs because the micropores are closed by the PE separator which melts at 125 °C ('separator shutdown').

#### 3.2.2. Overcharge

In the overcharge tests we carried out no fire or explosion was observed. Fig. 3 shows an example result of this test. The cell impedance increased suddenly in every test. This is due to the oxidation of the electrolyte with a low charging current (Fig. 3) or due to the separator melting with a high charging

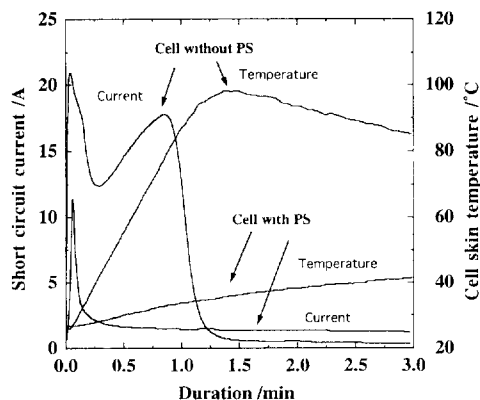


Fig. 2. Result of external short-circuit tests at room temperature for AA-size  $\text{Li/a-V}_2\text{O}_5$  cells with or without a Polyswitch (PS)

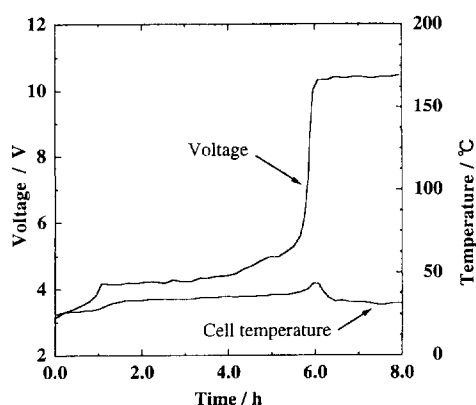


Fig. 3. Result of overcharge tests at room temperature for AA-size  $\text{Li/a-V}_2\text{O}_5$  cells, current = 200 mA, and compliance voltage = 10 V

current of more than 600 mA. In practical applications, an electronic device should be used to provide overcharge protection and ensure complete safety. After the separator has shut down, the separator has softened, and there still is a potential hazard caused by a reduction in impedance resulting from the complete liquidation of a PE separator, with further increase in cell temperature during continuous overcharge [2].

### 3.2.3. Forced discharge

Forced discharge test is carried out using a four-cell pack consisting of three cells of 3.3 V and one cell of 1.5 V connected in series. The four-cells pack is expected to be used for portable equipments working at 6 V. Lithium is not consumed uniformly at the anode during cycling. When we disassembled a cell after cycling at an early stage of cell development, we found that more lithium was consumed at the line where the anode lithium faces the wound end of the cathode sheet, as shown in Fig. 4. This phenomenon is caused by the so-called 'edge effect'. When pure Li foil is used as an anode, a forced discharge may cause significant heating leading to a fire due to a drastic reduction in the anode surface to about one tenth of its original area as a result of the Li being undercut by the edge effect. As shown in Table 2, our cell does not ignite or explode. This is because the anode has

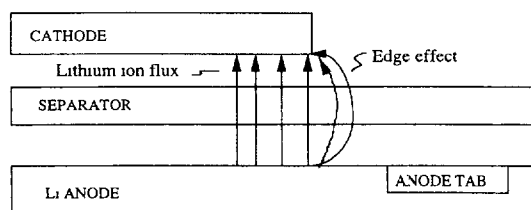


Fig. 4. Lithium anode cut at the end of the cathode during cycling

a copper substrate which prevents it from being cut by the cell [7].

### 3.2.4. Nail penetration

The nail penetration test is very important and is considered to simulate an internal short in a cell. Many accidents, involving fire have occurred in commercial lithium primary and secondary batteries which were caused by internal shorts. The internal short may be caused by a manufacturing defect such as a small conductive particle wound in the jelly roll, a wrinkle in the separator, or the poor alignment of a winding. No electronic device can protect against an internal short, and therefore the cell itself must pass this test. As shown in Table 2, our cells did not ignite or explode. In addition to the above, there is another potential cause for internal short, e.g. a lithium dendrite short. However, from our AA-cell data, a dendrite short will not occur if the discharge current is higher than 200 mA (approximately  $1 \text{ mA/cm}^2$ ).

### 3.2.5. Crush

The cell should also be able to survive a crush test because an electronic device cannot provide protection in this case either. As shown in Table 2, our test cell remained safe in crush tests both with a bar, and with a flat plate, which is an easier test to pass. This result is closely related to the jelly roll electrode configuration of our cell [2].

### 3.2.6. Heating

The heating test is very useful for evaluating the thermal stability of the cell. This test is carried out by increasing the temperature at a rate of  $5^\circ\text{C}/\text{min}$  and then holding it constant

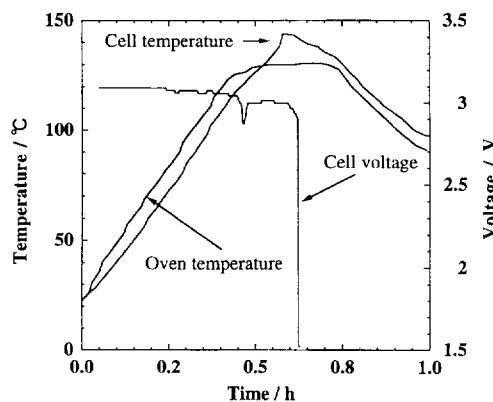


Fig. 5. Result of a heating test at  $150^\circ\text{C}$  for an AA-size  $\text{Li/a-V}_2\text{O}_5$  cell cycled 150 times with a 1000 mA discharge and a 200 mA charge between 1.5 and 3.3 V

at least until the maximum cell temperature induced by the internal exothermic reactions starts to decrease. Fig. 5 shows the result of a heating test. We have to be careful whether the thermal stability of the cell decreases with cycling when estimating the safety. The thermal stability of our cell is defined by the maximum temperature at which it can be ensured that no fire will occur. For our cell, this is at 130 °C before cycling. The thermal stability limit becomes even higher after cycling. These results are considered to be closely related to the increase in thermal stability of a lithium anode with an increase in charge/discharge cycle number as the result of the formation of a special lithium surface film containing vanadium [8]. This is different from the film usually formed in lithium metal cells by the reaction between the electrolyte and lithium [9].

#### 4. Conclusions

We have developed an AA Li/a-V<sub>2</sub>O<sub>5</sub> cell and the preliminary safety tests described were carried out for both fresh

and cycled cells. Based on these safety test results, it will be possible, with further research, to develop a rechargeable cell with a lithium metal anode which is sufficiently safe for practical use.

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