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Safety evaluation of rechargeable cells with lithium metal anodes and amorphous V_2O_5 cathodes

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Rechargeable cells with lithium metal anodes have a very large theoretical energy density and are a promising cell system. However, rechargeable lithium metal cells are not yet currently commercially available. One of the biggest problems with the cells is the poor safety aspect resulting from the high chemical reactivity of lithium. We have been studying a cell system consisting of an amorphous (a-)V_2O_5–P_2O_5 (95 : 5 in molar ratio) cathode, a lithium (Li) metal anode and an organic electrolyte in fabricating an AA-size prototype. In this paper, we report recent progress on our rechargeable lithium metal cell focusing on its safety.

Keywords: *lithium metal anode*, *rechargeable cell*, *safety*, *organic electrolyte*, *vanadium oxide*

1. Introduction

Lithium metal used as an anode active material has a very high theoretical capacity of 3860 Ah kg^{-1}, which is the highest among metallic anode materials. In addition, the standard electrode potential of lithium is high (−3.045 V vs SHE). This makes lithium metal a very attractive anode material. In 1958 Harris discovered that lithium was apparently stable in some organic solvents [1]. His finding showed the possibility of developing lithium batteries with a nonaqueous electrolyte.

Nonaqueous lithium secondary battery systems are being extensively investigated and several coin-type cells are now commercially available [2]. With regard to high capacity lithium secondary cells such as AA-size or larger, many prototype cells with different cell chemistries have been constructed and evaluated worldwide [3]. The Li/MoS_2 systems developed by Moli Energy was recalled because of an incident in 1989 when a cell caught fire. Since then, almost all lithium metal cell development has stopped because of safety problems. Just after the accident, a safer lithium cell, the lithium ion cell, was developed and is now commercially available.

However, the high energy density of lithium metals cells is still very attractive, if the safety problem can be overcome. We investigate the safety aspect from a scientific viewpoint, and estimate the possibility of developing a practical cell.

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2. Experimental details

2.1. *Configuration of prototype cells*

The conductivity of the nonaqueous electrolyte used in the AA-size lithium metal anode prototype cells is one order of magnitude lower than that of an aqueous system. Thus, thin electrodes are wound in a so-called 'jelly roll' configuration to increase the electrode area and thereby provide a cell with a high rate capability.

Amorphous (a-)V_2O_5 was used as the cathode active material [6]. To obtain V_2O_5 in an amorphous state easily, we mixed it with a small amount of P_2O_5. Figure 1 shows the long term cycleability of a-V_2O_5 in a laboratory coin-type cell with a large excess of lithium. a-V_2O_5 was able to undergo more than 4000 cycles with a minimal capacity fading rate. An a-V_2O_5 cathode, comprising a-V_2O_5, carbon and polymer binder, was coated and pressed on aluminium foil by the conventional slurry coating method. $LiAsF_6$/ethylene carbonate-based mixed electrolyte [5] was used because of its high lithium cycling efficiency and its high lithium ion conductivity. A micro porous polyethylene film was used as a separator.

3. Results and discussion

3.1. *Cell performance*

The performance of the prototype AA cell is shown in Table 1.

The cell has 2 Wh of energy and its maximum discharge current is 2 A which is limited by a Polyswitch (trademark name of the Raychem Co., thermal and current fuse) in the cell. The rate capability is

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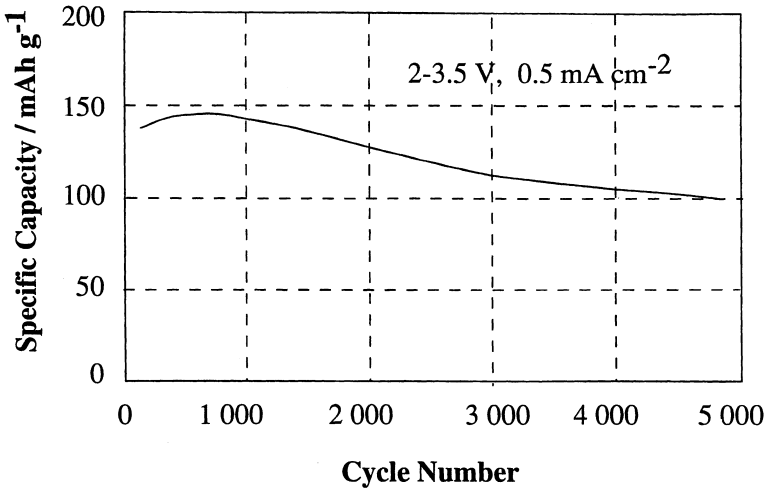

Fig. 1. Long term cyclability of a-V_2O_5 cathode, cycled between 2 and 3.5 V, 0.5 mA cm^{-2}.

Table 1. Performance of AA-size Li/amorphous V_2O_5 cell

Volume, mass	8 cm^3, 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^{-1}, 250 Wh dm^{-3}
Cycle life	150–300 cycles
Self- discharge rate	1% per month at 21 °C

shown in Fig. 2. The cycle life depends on both the charge and discharge current as with other lithium metal anode cells. As the discharge current increases, the cycling life tends to decrease. As regards charging, the life decreases as the charge current increases. We recommend a 200 mA charge, because a long charge time is impractical.

The results of safety tests are summarized in Table 2. In the following section, we describe the technology we used to improve safety.

3.2. *Heat generation in a cell*

Cell temperature is determined by the balance between the amount of heat generated in a cell and the amount dissipated outside the cell. Heat generation in a cell is caused by the thermal decomposition and/or reaction of the materials in the cell, listed below:

(i) Reaction between the electrolyte and the anode
(ii) Thermal decomposition of the electrolyte
(iii) Reaction between the electrolyte and the cathode
(iv) Thermal decomposition of the anode
(v) Thermal decomposition of the cathode.

When a cell is heated by a given trigger (e.g., an internal short, high current application or overcharge), heat will be generated as described above, if the cell temperature is high enough to cause the decomposition and/or a reaction. This situation leads to the thermal run-away of the cell. If little additional heat is generated, the cell temperature does not increase, and the cell is safer.

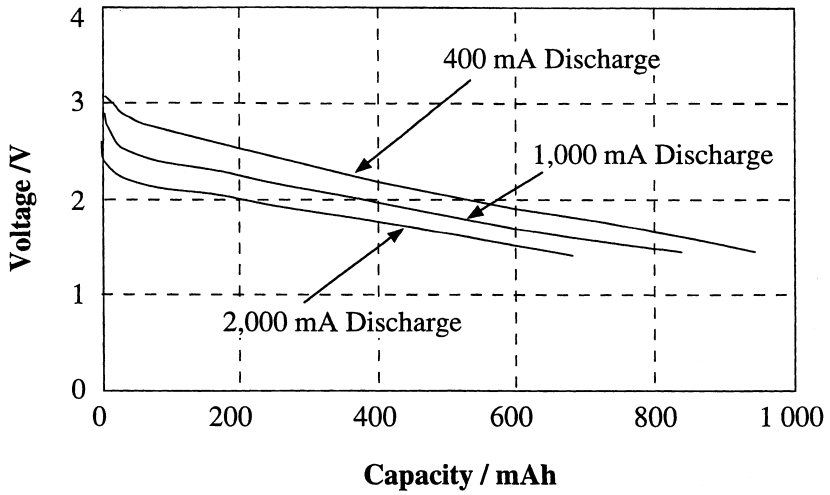

Fig. 2. Rate capability of AA-size Li/a-V_2O_5 cell.

Table 2. Safety test results for AA-size Li/amorphous V_2O_5 cell

(Precycling conditions; charge current 200 mA; discharge current and cycling number shown in Table)

Abuse test	*Test conditions*		*Results* (○; *no fire*)				
			Fresh cell	*Discharge current*			
				1000 mA *Times cycled*		400 mA	
				75	150	60	120
External short	Room temp (RT)		○	○	○	○	○
	40 °C		○	○	○	○	○
Forced discharge*	RT		○	○	○	○	○
	40 °C		○	○	○	○	○
Overcharge	Charge at 200 mA	RT	○	○	○	○	○
		40 °C	○	○	○	○	○
	Charge at 600 mA	RT	○	○	○	○	○
		40 °C	○	○	○	○	○
Crush	RT, round bar		○	○	○	○	○
	RT, flat plate		○	○	○	○	○
Nail penetration	RT		○	○	○	○	○
Thermal stability (Max. safe temp.)	5 °C min^{-1} held at a certain temp.		130 °C	150 °C	150 °C	140 °C	130 °C

Short test of 4-cell pack connected in series: three cells are in a fully charged state; one cell is discharged to 1.5 V.

3.2.1. Reaction between electrolyte and anode. Although the reaction between an electrolyte and lithium metal is suppressed by a passivating film on the surface of the lithium anode, they react when the temperature increases rapidly. This is because the thickness of the passivating film is not sufficient to prevent the reaction at elevated temperatures. The reaction continues until the passivating film reaches a certain thickness. The reaction is exothermic, so it increases the cell temperature. This situation occurs during a cell heating test. The cell is placed in an oven, in which the air temperature is raised to a certain temperature. As shown in Fig. 3, the cell temperature becomes higher than the ambient air temperature. This higher temperature is mainly caused by the reaction between the electrolyte and lithium metal, because the cell temperature finally returns to an ambient level.

3.2.2. Thermal decomposition of electrolyte. When an electrolyte is heated, it decomposes at a certain temperature with heat generation. The decomposition temperature depends on the materials used in the electrolyte. Some electrolytes decompose at 150 °C and this effect is lowered by cathode oxidation [7].

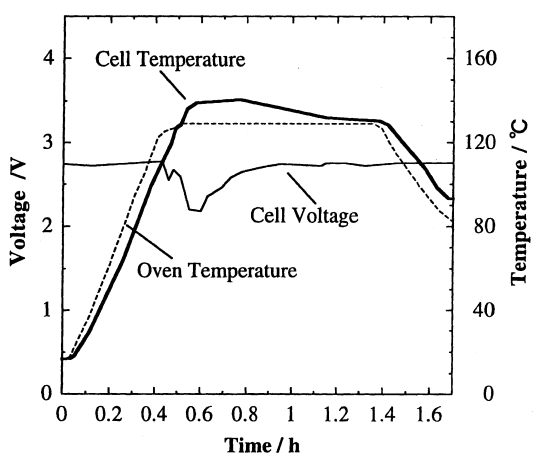

Fig. 3. Cell temperature during heating test.

3.2.3. Reaction between electrolyte and cathode. Usually, an electrolyte is selected for a cell on the basis of its having a higher decomposition voltage than the cathode voltage, so that they rarely react. One case where the reaction between electrolyte and cathode may occur is overcharging, where the electrolyte is oxidized with heat generation [8].

3.2.4. Thermal decomposition of anode. Lithium metal melts at 180 °C (endothermic). This poses no problems with a lithium metal cell. However, molten lithium should be carefully considered in terms of its reactivity and mobility leading to an internal short.

3.2.5. Thermal decomposition of cathode. 4 V cathodes ($LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$) are unstable especially when in a charged state [9]. Some of them decompose even at 180 °C. Although the voltage is lower, a-V_2O_5 is a safer cathode because it melts at 690 °C and decomposes at 1750 °C.

3.3. *Incidents during normal cycling*

We have been undertaking cycling tests with lithium metal anode AA size cells since 1985. At the beginning of our study, there were incidents during normal cycling tests. These incidents occurred at a probability of around 1%. We now consider these incidents to have occurred for the following reasons.

3.4. *Lithium anode cut at end of cathode*

Lithium is not consumed uniformly at an anode during cycling. When we disassemble a cell after

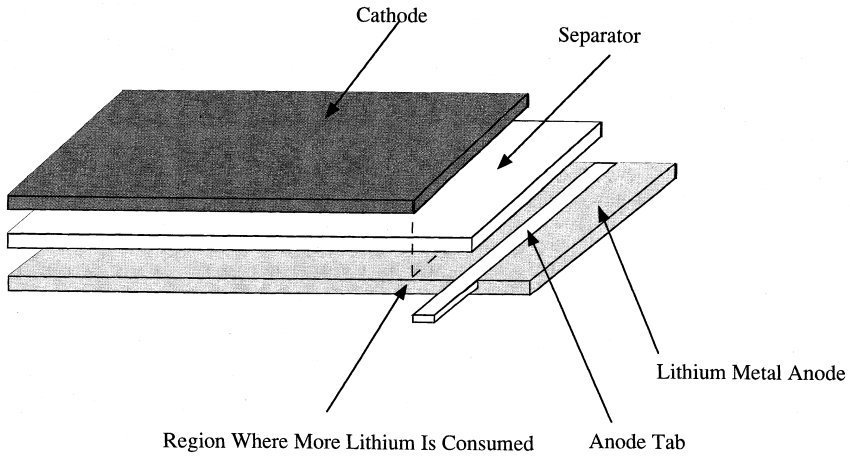

Fig. 4. Lithium anode cut at end of cathode during cycling.

cycling, we sometimes find that more lithium is consumed along the line where the anode lithium faces the winding end of the cathode sheet, as shown in Fig. 4. This is caused by the so-called edge effect. A larger current passes at the edge of an electrode than at other parts, because ions in the electrolyte can move outside the electrode to reach the end. When the anode is cut by the edge effect during cycling, its surface area decreases to about one tenth. Then there is a very large current density at the anode and this heats up the cell. To confirm this, we made a cell with an anode cut along the above line. The separator of the cell was found to be burned after discharge.

To avoid this cutting of the anode, we are using a lithium sheet with a copper substrate [10]. However, this reduces the cycling life by 25%. The cycling life of our cell with a pure lithium anode (no copper substrate) is shown in Fig. 5.

3.5. *Anode tab disconnection during cycling*

As shown in Fig. 6, anode tab disconnection as a result of the edge effect is another possible reason for the above occurrence. In our cell, the anode tab is no longer facing the cathode.

3.6. *Internal short*

There is a possibility that an internal short may cause an accident. A nail penetration test is an effective way to assess the damage that the internal short might cause. If the cell smokes, catches fire or explodes as a result of the nail penetration test, we believe the cell to be unsuitable for commercial use. However, an internal short will increase the cell temperature to above 100 °C even if the cell passes the nail penetration test. So, it is recommended to try to reduce the probability itself.

An 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 bad alignment of winding. In addition to the above, the lithium metal anode cell may suffer from a lithium dendrite short. From our AA cell data, as shown in Table 3, a dendrite short will occur only if the discharge current is lower than 200 mA (1 mA cm^{-2}).

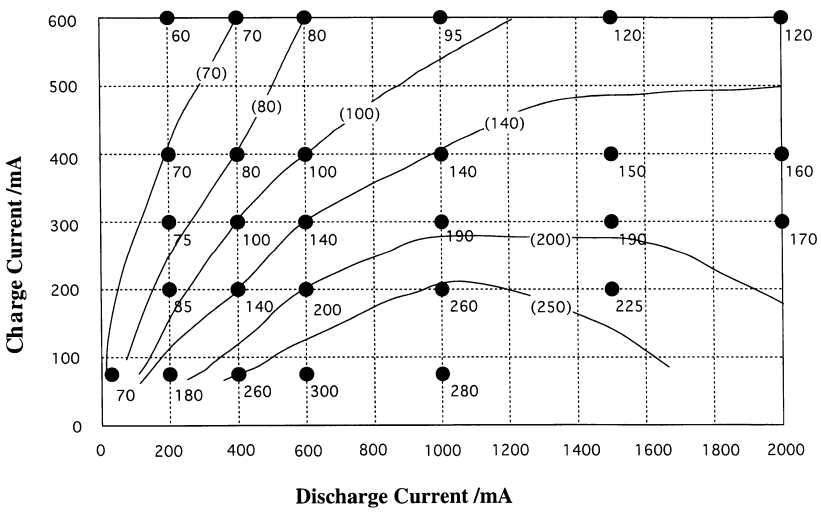

Fig. 5. Relationship between cycle life (●) and charge–discharge current.

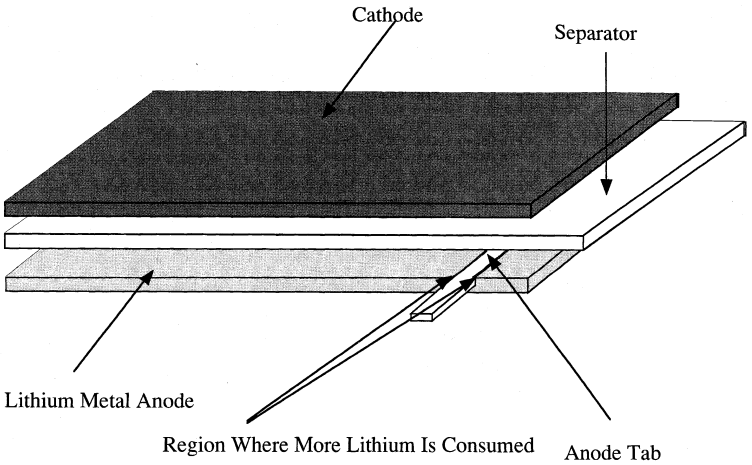

Fig. 6. Anode tab disconnection during cycling.

Table 3. Probability of dendrite short occurring during cycling depending on charge and discharge current

Discharge current/mA	*Charge current*/mA			
	200	300	400	600
40	2/2	2/2	2/2	2/2
200	0/2	0/2	0/2	0/2
400	0/2	0/2	0/2	0/2
600	0/2	0/2	0/2	0/2
1000	0/2	0/2	0/2	0/2
1500	0/1	0/1	0/1	0/1
2000	no data	0/1	0/1	0/1

3.7. *Safety tests on AA-size Li/a-V_2O_5 cells (Table 2)*

3.7.1. External short. As we are using a polyethylene separator and a Polyswitch, we have experienced no problems as regards external shorts.

3.7.2. Overcharge. We have overcharged cells to a very high degree. In every case, continued charging caused the cell to exhibit a sudden very high impedance. With a high charging current, the high impedance is caused by the separator melting. At a lower charge current, the high impedance is caused by electrolyte depletion as a result of cathode oxidation.

3.7.3. Forced discharge. A forced discharge will cut the anode lithium and the cell will become unsafe. We are using lithium with a copper substrate, thus improving the safety of the cell. The experimental results are shown in Table 4. We reduced the probability of a fire starting as the result of a forced discharge by using an anode with copper substrate.

3.7.4. Crushing. In our crush test we use a bar. The test using a plate is easier to pass and so we recommend the former.

3.7.5. Nail penetration. We use a 3 mm diameter nail. As mentioned before, this test is very useful for determining what happens during an internal short.

3.7.6. Thermal stability. This test is very useful for evaluating the thermal stability after cycling. If the thermal stability decreases after cycling, we have to estimate the safety carefully. Our cell is thermally stable up to 130 °C before cycling. Even after cycling, this thermal stability temperature is higher than 130 °C as shown in Table 2.

4. Conclusion

We have developed a 2 Wh class AA-size rechargeable Li/a-V_2O_5 cell. This cell weighs 18 g and delivers a nominal capacity of 900 mAh at 600 mA which lasts for 150–300 cycles, resulting in a high energy density of 110 Wh kg^{-1} or 250 Wh dm^{-3}. This cell can be discharged up to a rate of about 2 C. These are very attractive features for high rate discharge applications. A low self discharge rate of 1% per month is also a beneficial characteristic of this cell. Preliminary safety test results showed that this Li/a-V_2O_5 cell can be developed as a safe system.

Table 4. Results of forced discharge test

Current 3A, maximum voltage −10V, for 1h

Precycling before forced discharge test (Discharge current 40 mA, charge current 80 mA)	*Ratio of venting for cells with pure lithium anodes*	*Ratio of venting for cells with lithium/Cu/lithium anodes*
10 cycles (0 °C)	1/4	0/11
25 cycles (21 °C)	9/9	5/12

References

[1] W. R. Harris: PhD thesis, University of California, Berkeley (1958).

[2] Z. Takehara: Proceedings of the international workshop on 'Advanced batteries', Osaka, Japan (1995), pp. 1–11.

[3] T. C. Murphy, D. M. Cason-Smith, S. D. James and P. H. Smith, Proceedings of the 34th international 'Power Sources' symposium, Cherry Hill (1990) pp. 176–80.

[4] Y. Sakurai and J. Yamaki, *J. Electrochem. Soc.* **132** (1985) 512.

[5] S. Tobishima, M. Arakawa, T. Hirai and J. Yamaki: *US patent 4 737 424* (1988).

[6] Y. Sakurai, S. Sugihara, M. Shibata and J. Yamaki, *NTT Review* **7** (1995) 60.

[7] M. A. Gee and F. C. Laman, *J. Electrochem. Soc.* **140** (1993) L53.

[8] F. C. Laman, Y. Sakurai, T. Hirai, J. Yamaki and S. Tobishima, Extended abstract of the sixth international meeting of 'Lithium Batteries', III-A-01 (1992).

[9] D. Fouchard, L. Xie. W. Ebner and S. Megahed, Proceedings of 186th ECS meeting (1994).

[10] T. Hirai and J. Yamaki, *US patent 5 368 958* (1994).