

## Experimental studies of ultra-thin lithium batteries

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### Abstract

$\text{Li}_{1+x}\text{V}_3\text{O}_8$  cathode film was prepared by casting. The film is soft with high mechanical strength, long-term stability and insensitive to moisture. Single and double cathode ultra-thin lithium batteries were assembled utilizing the above-mentioned film as cathode, and discharge tests were performed. Results show that double cathodes might increase the cell capacity.

### Introduction

Great progress has been made in the development of lithium batteries [1–4], towards the target of fabrication of high energy density (or high power density) cells. At present, common Li batteries using powder-pressed pellets as cathodes have the following drawbacks [5]: in the region of the cathode that is not in contact with the electrolyte, they are starved of electrolyte. For this reason the active material may not be fully utilized. As a consequence, it is difficult to obtain high energy density. In order to obtain high energy density cells, two problems must be solved: (i) the utilization factor of cathode-active material should be elevated, and (ii) the weight of the battery should be reduced. The effective solution to these problems is thinning (or ultra-thinning) of Li batteries.

Since the solid-state electrolyte thin film can already be fabricated, the remaining key technique for Li battery ultra-thinning is cathode thinning, therefore many scientists are developing high-quality cathode films. We have prepared successfully cathode films of various materials, e.g.  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ ,  $\text{LiVO}_2$ ,  $\text{LiV}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$  and  $\text{Na}_{1+x}\text{V}_3\text{O}_8$ , etc. The utilization of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  as a secondary Li battery cathode is advantageous for easy synthesis and achievement of high energy density. Therefore a brief introduction on the preparation and properties of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  film and on the application of this film as a cathode in ultra-thin Li batteries are presented in this article.

### Experimental

#### *Preparation and test of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ film*

The film was prepared by 'casting' [6, 7]. The weights of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , PEO (polyethylene oxide) and acetylene black were taken in percentage as 48, 39 and 13%.

The mixture was completely dissolved in acetonitrile, cast into the mould in a dry glove box and when the solvents had evaporated and the material dried, the product fabrication is completed. The periphery of a 60 mm diameter, 60–100  $\mu\text{m}$  thickness  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  film was gripped by a clamp, then weights were added to it. When the weights increased to 550 g, the film stretched without fragmentation. After exposure of the film in air for three months, no significant variations resulted in softness, sensitive to moisture, open-circuit voltage and X-ray diffraction spectrum.

#### Test of 0.4–0.6 mm ultra-thin lithium batteries

A schematic diagram of the ultra-thin Li battery is shown in Fig. 1 (technique is given in detail in refs. 8, 9. The cathode is  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  film and filter paper containing 1 M  $\text{LiClO}_4/\text{PC}$  liquid electrolyte served as isolator. Figure 2 is the schematic diagram of double-cathode cell, two cathodes located symmetrically on both sides of the anode. In Fig. 3, curves 1, 2 and 3 are cell discharge curves assigned to acetylene black contents in cathode films with a percentage 0, 22, and 13%, respectively. Figure 4 presents discharge curves of cells with brittle and soft cathode films. The cathodes of the following four cells were cut from a single film. Cell 1 has one film utilized as cathode, the cathode of 2 is composed of two layered films. Cell discharge characteristics of cells 1, 2, 3 and 4 are indicated by 1, 2, 3 and 4 in Fig. 5. Voltage recovery appeared in all the above-mentioned cells with thin-film cathodes and their curves are similar to that shown by 1 in Fig. 6. Voltage recovery also appeared in a cell with a cathode made by powder-pressed pellet [10], as shown by 2.



Fig. 1. Schematic diagram of the structure of an ultra-thin lithium battery: (1) anode current collector; (2) anode lithium; (3) isolator; (4) cathode film; (5) cathode current collector, and (6) glue.

Fig. 2. Ultra-thin lithium battery with double cathodes: (1) cathode current collector; (2) cathode film; (3) isolator; (4) anode lithium; (5) glue, and (6) anode current collector.

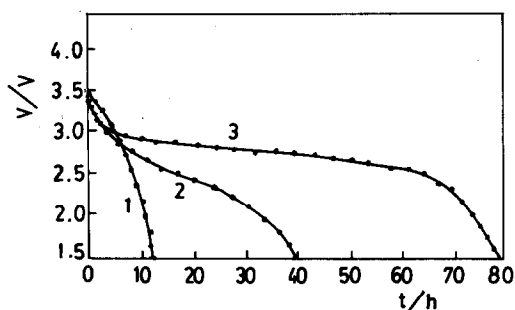


Fig. 3. Discharge curves of an ultra-thin lithium battery; acetylene black content (1) 0%, (2) 22%, and (3) 13%; constant discharge current: 20  $\mu\text{A}$ .

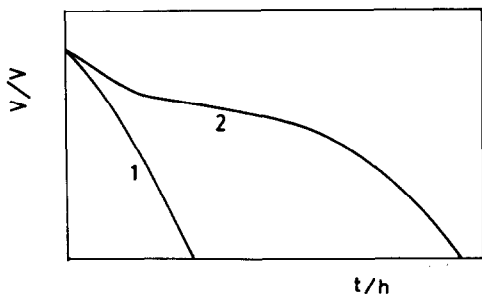


Fig. 4. Discharge curves of ultra-thin batteries with cathode films having various mechanical strength: (1) brittle cathode film, and (2) soft and elastic cathode film.

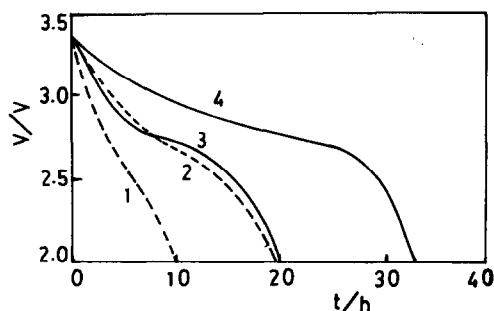


Fig. 5. Comparison of discharge curves of ultra-thin lithium batteries with single and double cathodes: (1) cell with one-cathode film; (2) cell with two-cathode films; (3) double-cathode cell with one film as cathode, and (4) double-cathode cell with two films as cathode; constant discharge current:  $100 \mu\text{A}$ .

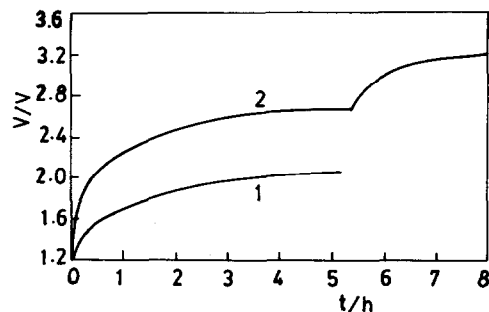


Fig. 6. Curves of self-recovery voltage of lithium batteries: (1) cell with thin-film cathode, and (2) cell with powder-pressed pellet as cathode.

## Results and discussion

All the areas of the cathode film of the cells were  $1 \text{ cm}^2$ , discharged at a constant current, to a cutoff voltage of 2 V. Figure 3 shows that the capacity of the cell without acetylene black is the minimum, that with acetylene black content 13% is the maximum. The reason is: in the film cathode, the active material can be fully utilized, so that the capacity of cells having most active material is greatest. After adding acetylene

black, on the one hand acetylene black diffuses into the vacancies between the crystallites, thus reducing the resistance and is favourable to electrical conduction and the capacity increases. On the other hand the proportion of active material is reduced, and the resulting capacity decreases. Thus it can be seen that an optimum amount of acetylene black should be applied. Figure 3 shows that a content of 13% is suitable.

Two curves in Fig. 4 show that the capacity of the cell using the soft and elastic film as cathode is larger than that of cell with brittle film. These phenomena appeared also in experiments for cells with cathodes using  $\text{MnO}_2$ ,  $\text{LiV}_2\text{O}_4$ ,  $\text{LiVO}_2$  and  $\text{V}_2\text{O}_5$  films (the results deviated only in different capacities, thus no unit was shown on coordinates in Fig. 4). Curves 1 and 2 in Fig. 5 are two of the tests of various cells with cathodes using one or two films. Capacity differs a little for various cells using two large films as cathodes, while capacity differs greatly for various cells using single film as cathode. The average result of the multitest implies that the capacity represented by curve 2 is about more than twice that represented by curve 1. This is because although cathode films are cut from the same film, inhomogeneity occurred due to topotactic nonuniform thickness (inhomogeneity in material content) in a large film. The probability of inhomogeneity is readily apparent in a small film, therefore the capacities of various cells differ greatly. For two layered films, this inhomogeneity might be compensated, and cell capacities differ less. Curves 3 and 4 are for the discharge of two cells with double cathodes and containing solid-state electrolyte; their capacities are 1.9 and 3.3 mA h, respectively. The capacity of cell 3 is larger than that of cell 2, and the capacity of cell 4 is less than twice that of cell 3. The reasons are: (i) using different electrolyte, and (ii) voltage difference occurred between the two cathodes and the anode in the double cathode cell. It can be seen from Fig. 6, at the beginning that the voltage recovered faster for the cell using powder-pressed pellet as cathode than that of the cell using thin-film cathode. This is because electrolyte starvation exists in the cathode using a powder-pressed pellet and the diffusion velocity of Li ions is smaller than that from the cathode using thin film, so that more ions condensed on the surface, and many vacancies occurred in the interior. After discontinuation of the discharge,  $\text{Li}^+$  ions on the surface can diffuse faster toward the interior, so that self-recovery voltage elevated faster initially. Voltage can be recovered to approximately 75% of open-circuit voltage after several hours.

## Conclusions

By means of the preceding experiments the following results are obtained:

- (i) cathode film is soft and elastic, with higher mechanical strength;
- (ii) film has a long-term stability;
- (iii) a suitable content of acetylene black is 13% in the cathode film;
- (iv) capacity fluctuation is little in a cell using two layered films as cathode, and
- (v) in order to obtain large capacity, a cell with double cathodes can still be used although the drawback of voltage asymmetry appeared.

## References

- 1 M. Gauthier, A. Belanger, B. Kapfer, G. Vassort and M. Armand, in J. R. MacCallum and C. A. Vincent (eds.), *Polymer Electrolyte Reviews* 2, Elsevier, London, 1989, p. 285.
- 2 G. Wang and G. Pistoia, *J. Electroanal. Chem.*, 302 (1991) 275.

- 3 D. Shackles, *4th Int. Seminar Lithium Battery Technology and Application, Mar. 6-8, 1989, Deerfield Beach, FL, USA.*
- 4 M. Z. A. Nunshi and B. B. Owens, *Solid State Ionics*, 26 (1988) 41.
- 5 G. Pistia, M. Pasquali, M. Tocci, V. Manev and R. V. Moshtev, *J. Power Sources*, 15 (1985) 13.
- 6 C. Carre, *Br. Polymer J.*, 20 (1988) 269.
- 7 K. M. Abraham, M. Alamgir and S. J. Perrotti, *J. Electrochem. Soc.*, 23 (1988) 535.
- 8 L. Zaihai, L. Limin and Z. Wenbin, *Proc. 5th Int. Meet. Lithium Batteries, Beijing, China, May 27-June 1, 1990*, p. 582.
- 9 L. Zaihai, L. Limin and Z. Wenbin, *Chin. Sci. Bull.*, 37 (1991) 1783.
- 10 L. Zaihai, Z. Wenbin and W. Gang, *Acta Phys. Sin.*, 39 (1990) 138.