Novel 2 V rocking-chair lithium battery based on nano-crystalline titanium dioxide

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Abstract

A novel type of 2 V rocking-chair lithium batteries with nano-crystalline TiO_2 (anatase) as the negative and $LiNi_{0.5}Co_{0.5}O_2$ as the positive electrode with $LiN(CF_3SO_2)_2$ + ethylene carbonate/dimethoxyethane electrolyte has been studied. The closed R921 button cells showed excellent cycling performance and a charge density of about 50 mAh/g. The advantages of the specific porous morphology of nano-crystalline insertion materials for Li insertion and release are discussed. © 1997 Elsevier Science S.A.

1. Introduction

While most of the attention of both the industry and research groups in the field of lithium batteries was focused in recent years on 4 V carbon rocking-chair systems, 2 V batteries seem to be more practical than their 4 V counterparts for application in micro-electronics and/or consumer devices with photovoltaic recharging, e.g. solar watches. This for the following two reasons: (i) lower voltage allows higher integration of microelectronic circuits, and (ii) the photovoltaic recharging system offers only a limited voltage.

This paper refers to a study on a new type of 2 V rocking-chair lithium battery with nano-crystalline TiO_2 (anatase) as the negative electrode and $LiNi_{0.5}Co_{0.5}O_2$ as the positive electrode.

2. Experimental

Nano-crystalline titanium dioxide powder (Bayer PKP 09040, anatase, purity > 99%) was used as received. The starting powder was characterized by X-ray diffraction (XRD) by using an X-ray diffractometer Siemens DS-500 with Cu Kα radiation. The morphology of the samples was analysed by scanning electron microscope (SEM) using a Hitachi S-900 instrument. The BET surface area was 154 m^2/g (Kr-isotherms, Accusorb 2100 E, Micrometrics).

$LiCoO_2$ and $LiNi_{0.5}Co_{0.5}O_2$ (Cyprus Foote Mineral) had both a particle size of about 400 nm and a surface area of 4 m^2/g.

Electrodes were prepared in the form of pressed pellets with 10% graphite (KS-10, Lonza) as the conducting agent and 2% polyvinylidene fluoride (PVDF) (Solef, Solvay) as the binder.

Ethylene carbonate (EC) and dimethoxyethane (DME) were from Tomiama. A 1:1 mixture (by mass) was dried over a 4 Å molecular sieve (Union Carbide). $LiN(CF_3SO_2)_2$ (Fluorad HQ 115 from 3 M) was dried at 200 °C and at 10^{-3} Pa. The prepared 1 M solution $LiN(CF_3SO_2)_2$ + EC/DME contained about 10 ppm of water. The preparation of the electrolyte and the assembling of the experimental button cells were performed in an argon-filled glove box (1–5 ppm H_2O, 1 ppm O_2).

Electrochemical experiments employed a convential three-electrode cell interfaced to a potentiostatic/galvanostatic setup (PAR EG&G 273 A). The reference and auxiliary electrodes were prepared from pure lithium metal. The closed R921 button cells were further tested at ambient temperature using a Maccor 2000 series battery test equipment.

3. Results and discussion

Fig. 1 shows the XRD pattern of the nano-crystalline TiO_2 (anatase) powder. The primary particle size, d, was calculated from the X-ray line width using the Scherrer formula
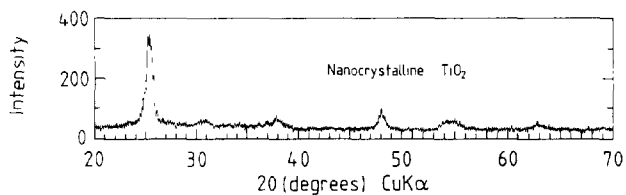
Fig. 1. XRD spectra of TiO₂ (anatase Bayer PKP 09040)

Fig. 2. SEM images of the nano-crystalline film of Bayer PKP 09040 TiO₂

$$d = 0.9\alpha / \beta_{1/2}\cos\theta \qquad (1)$$

where α is the X-ray wavelength, $\beta_{1/2}$ the corrected width of the main diffraction peak at half-height and θ the diffraction angle. The d value of TiO₂ Bayer PKP 09040 was 10 nm [1].

Fig. 2 shows the SEM images of the surface of TiO₂ (anatase). The particles are roughly spherical, the surface is highly textured with open pores and channels. The particle size is about 10–15 nm, in agreement with the XRD results.

4. Electrochemistry: Li⁺ insertion

In the Li⁺-containing electrolyte solutions and at potentials below the flatband, the insertion of Li⁺ into anatase takes place [1,2,4,5].
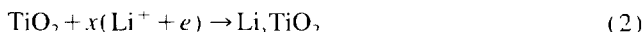
$$TiO_2 + x(Li^+ + e) \rightarrow Li_xTiO_2 \qquad (2)$$

Fig. 3 displays the galvanostatic charge/discharge characteristics of the TiO₂ and LiCoO₂ electrodes versus lithium metal in 1 M LiN(CF₃SO₂)₂ + EC/DME electrolyte solution. Screening of many combinations of lithium salts and aprotic solvents such as propylene carbonate (PC), DME, EC, dimethyl carbonate (DMC), diethyl carbonate (DEC),
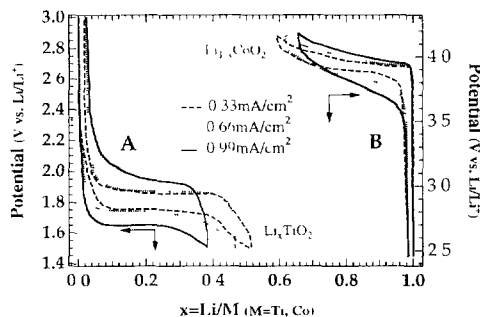

Fig. 3 Galvanostatic charge/discharge of the TiO₂ and LiCoO₂ electrodes in cell with a lithium counter electrode

LiCF₃SO₃, LiAsF₆ and LiPF₆ by cyclic voltametry [3] showed that 1 M LiN(CF₃SO₂)₂ + EC/DME exhibited the best insertions capacities, x, and insertion/extraction reversibilities [6].

The solutions in EC/DMC and EC/DEC showed better stability against anodic breakdown at potentials greater than 4 V, but the performance with the nano-crystalline TiO₂ electrode was lower which is presumably due to lower conductivity of these solutions.

Supposing that the Li⁺-insertion capacity is limited by the solid-state diffusion of Li⁺/TiO₂ as demonstrated in Fig. 4 we should find in nanosized anatase material the effective diffusion time, t.

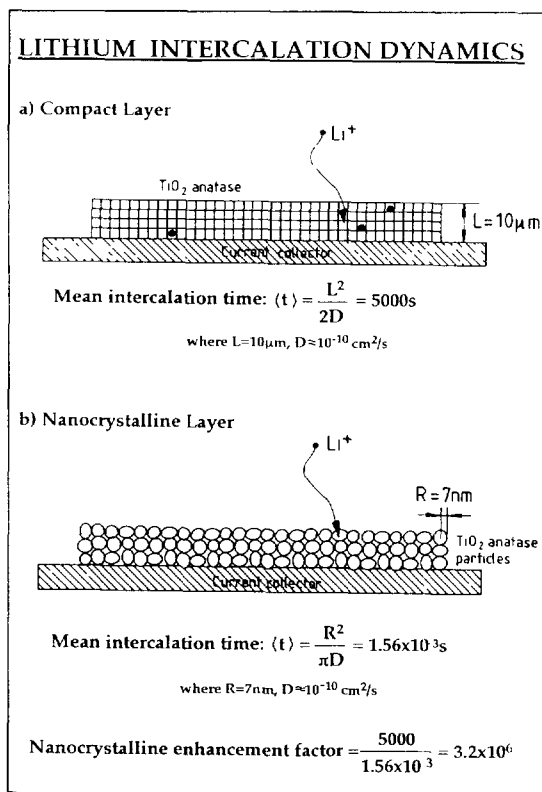$$t = R^2 / \pi D \cong 0.53 \text{ s} \qquad (3)$$

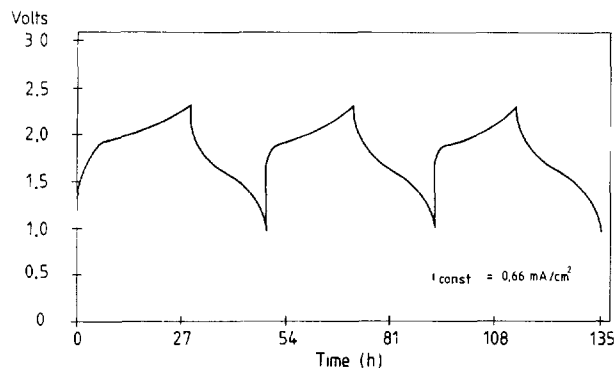Fig. 4. Diffusion model for conventional and nano-crystalline Li⁺-ion battery

Fig. 5. Galvanostatic charge/discharge of the $TiO_2/LiNi_{0.5}Co_{0.5}O_2$ button cell.
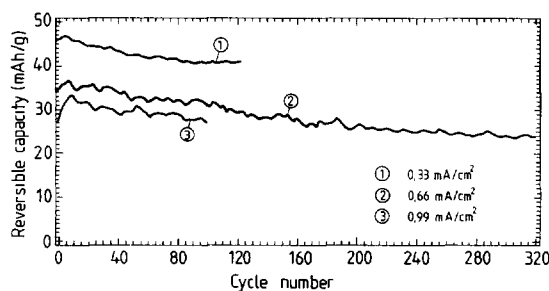

Fig 6 Cycling performance of the $TiO_2/LiNi_{0.5}O_2$ cell. The cell was periodically discharged (1.0–2.2 V) at constant current densities of 0.33, 0.66 and 0.99 mA/cm^2.

where D is diffusion coefficient of Li^+ in anatase $\cong 1.81 \times 10^{-13}$ cm^2/s and R is the particle radius $\cong 7$ nm. Nevertheless, the real insertion time of Li^+ is in order of magnitude higher than predicted by Eq. (3). We have recently suggested that the solid-state diffusion of Li^+ is not the rate-determining process and that the Li^+ insertion is controlled by the slow formation of an accumulation layer due to ohmic drops and electron trapping at the surface. Screening of many TiO_2-types with different morphology by galvanostatic chronopotentiometry showed that at relatively high charging rate there is some enhancement of the insertion ratio, x, and the reversibility (Eq. 1) with decreasing particle size of the insertion material. Kavan and co-workers [3,7] observed this effect in detail by electrochemical mesurements on thin TiO_2 films supported on SnO_2-coated glass. In prac-

tical $TiO_2/LiCo_{0.5}Ni_{0.5}O_2$ button cells we found that the optimal anatase particle size is about 10–15 nm.

The galvanostatic charge/discharge behaviour of the $TiO_2/LiNi_{0.5}Co_{0.5}O_2$ battery is shown in Fig. 5.

The completed crimp-sealed coin-type cell (diameter: 9.5 mm, height: 2.0 mm) delivered a reversible capacity of about 50 mAh/g (based on the mass of active electrode materials at ± 0.33 mA/cm^2 in the 1–2.2 V region) for over 300 cycles as shown in Fig. 6.

5. Conclusions

The investigated nano-crystalline TiO_2 (anatase) and $LiNi_{0.5}Co_{0.5}O_2$ system is an example of promising rechargeable 2 V rocking-chair batteries for low drain devices such as watches, computer memory backup, etc.

A standard size R921 coin cell supplied typically 3–5 mAh at ± 0.1–0.3 mA. The obtained charge density is about 50 mAh/g. The advantage of the nano-crystalline porous morphology of insertion materials is demonstrated in enhancement of the reversibility and insertion ratios.

Acknowledgements

References

[1] S.Y Huang, L Kavan, A. Kay, I. Exnar and M. Gratzel, Active and Passive Elec. Comp., 18 (1995) 23–30.
[2] S.Y. Huang, L. Kavan, I Exnar and M. Grätzel, J. Electrochem. Soc., 142 (1995) L142–144.
[3] L. Kavan, M Grätzel, J. Rathousky and A. Zukal, J. Electrochem. Soc, 143 (1996) 394
[4] T. Ohzuku and T Hirai, Electrochim. Acta, 27 (1982) 1263.
[5] T. Ohzuku and T Kodama, J. Power Sources, 14 (1985) 153.
[6] K. Kanamura, K. Yuasa and Z. Takehara, J Power Sources, 20 (1987) 127.
[7] L. Kavan, K. Kratochvilová and M. Gratzel, J Electroanal Chem., 394 (1995) 93