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High energy density, thin-film, rechargeable lithium batteries for marine field operations

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Abstract

All solid state, thin-film batteries with the cell configuration of VO_x /block copolymer electrolyte/Li have been designed, constructed, and tested. The additive-free (no carbon, no binder) cathode consisted of a dense film of vanadium oxide (~ 200 nm thick), deposited on aluminum foil and prepared by laser assisted vapor deposition of vanadium metal in an oxygen atmosphere of controlled chemical potential. The electrolyte was a block copolymer of poly[oligo(oxy-ethylene) methacrylate]-*b*-poly-(methyl methacrylate) [hence forth denoted as POEM-*b*-PMMA] containing LiCF_3SO_3 . The anode was metallic lithium. At room temperature, cathode capacities of ~ 395 mAh/g were measured at a current rate of $0.5C$ ($C = 400$ mA/g) over an operating voltage ranging from 1.5 to 4.0 V. The cathode proved to be resistant to capacity fade as evidenced by the small loss of discharge capacity during the extended cycling (over 200 cycles). It was possible to draw substantial currents. Routine testing was conducted at $0.5C$; however, discharge rates as high as $1.6C$ were achieved. Based upon these results, cells designed with these materials in optimal dimensions are projected to have energy densities exceeding ~ 350 Wh/kg and power densities exceeding 560 W/kg at $1.6C$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium polymer battery; Vanadium oxide; Block copolymer; Microbattery

1. Introduction

For the operation of sensory enhancement equipment, automatic weapons, communications systems, etc. portable electrical power is an essential element for marines in field operations. With projected practical energy densities exceeding 300 Wh/kg, low safety risks and great flexibility in battery configuration, the lithium polymer battery (LPB) is an attractive option for the distributed power storage needs of soldiers. For underwater missions the LPB has the added advantages of pressure tolerance and near neutral buoyancy. However, a number of materials and processing challenges must still be overcome to achieve these performance advantages. The purpose of the present study was to determine the performance limits of a thin-film battery comprising an additive-free (no carbon, no binder) oxide cathode, a solid polymer electrolyte, and a metallic lithium anode.

2. Experimental

Vanadium oxide (VO_x) thin films were deposited onto an aluminum foil substrate (area ~ 1 cm², thickness ~ 20 μm) by laser-assisted vapor deposition in an oxygen atmosphere of controlled chemical potential (air at a reduced total pressure of 0.5 atm). Films were annealed at 250°C for 2 h. Oxide film thickness was measured with a DekTak profilometer and determined to be ~ 0.2 μm . The films were characterized by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (Rigaku RTP500RC) and were found to be X-ray amorphous.

The block copolymer electrolyte (BCE), measuring about 100 μm in thickness, consisted of 77 wt.% PMMA-*b*-POEM (32:68) + 23 wt.% polyethylene glycol dimethyl ether (PEGDME, $M = 430$ g/mol, Polysciences) doped with LiCF_3SO_3 (EO:Li⁺ = 20:1) and was prepared by solution casting. The synthesis of the block copolymer PMMA-*b*-POEM has been described elsewhere [1].

The test cell comprised a cathode of VO_x on aluminum foil and an anode of lithium on a copper current collector separated by the BCE film. Cycle testing was conducted at

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25°C with a MACCOR series 4000 automated test system. Voltage limits were set at 4.0 and 1.5 V, while discharge/charge rates ranged from 0.5 to 1.6C, where the C/1 rate is defined as a current density of $I_c = I_d = 400$ mA/g cathode mass.

3. Results and discussion

Fig. 1 shows the first 12 cycles at a current density of 200 mA/g. The cathode discharge capacity is about 395 mAh/g, which corresponds to ~ 0.9 Li per mole of VO_x when the calculation assumes V_2O_5 stoichiometry. This battery shows fairly good coulombic efficiency as can be seen from the small difference between the discharge and charging capacities. This coulombic efficiency is one of the reasons that the thin-film battery exhibits excellent long-term stability. Furthermore, the polymer electrolyte used in our cell is known to have a very wide stability window (up to 5.0 V with respect to metallic lithium) [1]. Consequently, an all solid state device employing BCE as a solid electrolyte is expected to exhibit a better coulombic efficiency than would a cell with liquid electrolyte.

Fig. 2 shows long-term cycle testing results for the same cell. Again the current density was set at $I_c = I_d = 200$ mA/g with voltage limits of 1.5 and 4.0 V. The cell exhibits very low capacity fade from the 2nd cycle to beyond the 50th cycle. The degradation of reversible charge capacity during the 1st cycle is common to most electrode materials and may be attributed to side reactions between the electrode and the electrolyte.

Charge/discharge tests were conducted at various current densities, all at room temperature. A fresh cell was cycled 50 times between 1.5 and 4.0 V at $I_c = I_d = 200$ mA/g, followed by 10 cycles at $I_c = 200$ mA/g, $I_d = 400$ mA/g, followed by cycling at $I_c = 200$ mA/g, $I_d = 640$ mA/g. Fig. 3 shows the discharge capacities thus obtained. At 200 mA/g a discharge capacity of ~ 395 mAh/g and an energy density of ~ 1090 Wh/kg were measured. As expected, with increasing current density there is a corre-

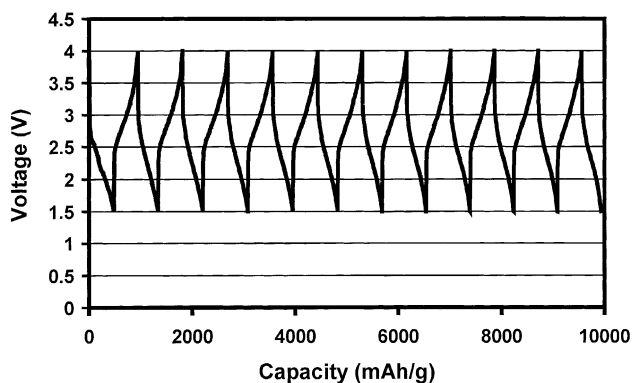


Fig. 1. Charge/discharge curve of $\text{VO}_x/\text{BCE}/\text{Li}$ cell, cycled between 1.5 and 4.0 V at a current density of 200 mA/g.

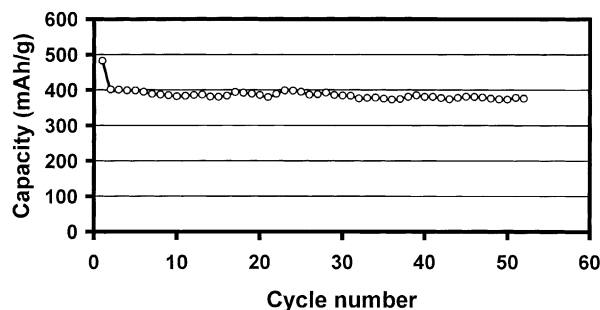


Fig. 2. Cyclic testing of $\text{VO}_x/\text{BCE}/\text{Li}$ cell. Current density = 200 mA/g. Voltage range = 4.0 > V > 1.5 V.

sponding decrease in discharge capacity. At 640 mA/g, a discharge capacity of ~ 310 mAh/g and an energy density of ~ 850 Wh/kg are measured. However, the discharge capacity obtained at 1.6C (~ 310 mAh/g) is more than 78% of the capacity (395 mAh/g) obtained at 0.5C. Importantly, when the discharge current density was lowered to 200 mA/g after 200 cycles, the discharge capacity increased to about 370 mA/g at this rate, demonstrating the excellent reversibility of this battery.

These data indicate fairly fast lithium intercalation kinetics within the vanadium oxide cathode, and only a small ohmic drop across the BCE. It is known that the rate capability of a lithium battery is often limited by solid state diffusion of lithium ions into the intercalation electrodes. Hence, the reduction in length scale afforded by the thin-film nature of this battery proved to be advantageous.

Based upon these results, we have designed a thin film microbattery containing the following elements chosen to have optimal dimensions:

- **Cathode:** dense VO_x film on aluminum current collector.
- **Electrolyte:** block copolymer of poly[oligo(oxy-ethylene) methacrylate]-*b*-poly(methyl methacrylate) [POEM-*b*-PMMA] containing LiCF_3SO_3 .

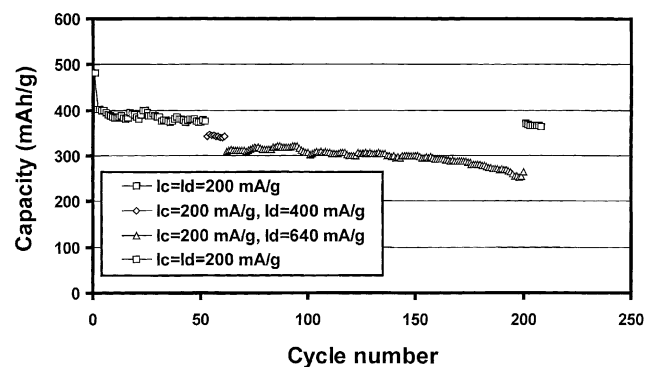


Fig. 3. Rate capability tests of $\text{VO}_x/\text{BCE}/\text{Li}$. The charge current density was constant across all cycles ($I_c = 200$ mA/g), while discharge rates were varied. The discharge current density was kept at 200 mA/g for 50 cycles, increased to 400 mA/g for 10 cycles, followed by 640 mA/g for an additional 160 cycles, and finally returned to $I_d = 200$ mA/g for 10 more cycles. Voltage range = 4.0 > V > 1.5 V.

- *Anode*: metallic lithium on copper current collector.
- *Wrapper*: PET.

The resultant device is projected to have energy densities exceeding ~ 350 Wh/kg and power densities exceeding 560 W/kg, both reported at 1.6C.

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