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Journal of Power Sources 92 (2001) 120–123

JOURNAL OF
POWER
SOURCES

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Lithium batteries composed of aluminate polymer complexes as single-ion conductive solid electrolytes[☆]

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Received 24 September 1999; received in revised form 7 April 2000; accepted 24 May 2000

Abstract

Single-ionic conductors, which display lithium ion migration exclusively (without anion migration), have been realized as the polymeric solid electrolytes with lithium orthoaluminate repeating units carrying oligo(oxyethylene) main chain and two side chains of endomethoxy{oligo(oxyethylene)}. The ionic conductivity of the aluminate polymer complexes is about 10^{-6} – 10^{-7} S/cm at room temperature. Thin film lithium secondary batteries were fabricated into 5.5 cm×4.5 cm×0.02–0.03 cm (thick) cells from lithium foil (anode), aluminate polymer complex (electrolyte) and TiS₂ (cathode). These batteries show minimal decay of output voltage upon constant current discharging and their capacity of first cycle was about 146 mA h/g of active cathode material. By contrast typical bi-ionic conductor of (aluminate polymer complex+5% LiClO₄) hybrid system showed, on the contrary, rapid decay of output voltage, due to polarization. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aluminate complex; Ionic conduction; TiS₂; Polymer complex; Solid electrolyte

1. Introduction

Because of their remarkably high voltage or high energy density lithium ion batteries were recently incorporated into cellular or notebook type personal computers. As shown in Fig. 1, these batteries can be classified into three categories by the type of ion transport through the electrolyte layer and ingress/egress of ions to/from the electrodes during the charging/discharging processes. For example, (1) a metallic lithium anode coupled with chalcogenide cathodes such as, (Li/electrolyte/TiS₂), (2) a lithium-ion intercalation compound anode coupled with metaloxide cathode such as, (graphite-Li/electrolyte/Li_x(CoO₂)_y), and (3) a metallic lithium anode coupled with p-type doped polymer conductor cathodes such as, (Li/electrolyte/poly(aniline)⁺X⁻). In batteries of types (1) and (2), both electrodes are active to ingress or egress of lithium ion but inert to those of anions, X⁻ migration is not necessary. Single-ionic conductors with the large lithium ion transport number, i.e., $t_+ \cong 1$ and $t_- \cong 0$, are preferable as the electrolyte. Otherwise, severe polarization that is brought about by the localization of X⁻ nearby the anode may decrease the cell performance when ordinary

bi-ionic conductors are employed. In order to realize the single-ionic conduction, the present authors fixed anionic sites to polymer chains [1–3] to diminish the diffusion of anionic species through the electrolyte films. The first single ion conductors, lithium carboxylate [2] and sulfonate [3] with oligo(oxyethylene) side-chains gave but very low conductivity, 10^{-8} S/cm, due to large ion-dissociation energy. The large impedance of these single-ionic conductors did not allow to fabricate rechargeable batteries with satisfactory current output. In order to decrease the dissociation energy, Benrabah et. al. have changed the anionic moiety into perfluorosulfonate units attached to network polyester chains [4] and Shriver and co-workers have chosen the orthoaluminate anion with large ionic radius and demonstrated sodium single-ionic polymer complexes [5,6] followed by the lithium ion conductive poly(aluminosilicate) with the ionic conductivity of about 10^{-5} – 10^{-6} S/cm [7]. Subsequently, we reported lithium ion conductive tetraalkoxy aluminate polymer complexes [8] (Fig. 2) and thioaluminate polymer complexes [9] with relatively high ionic conductivity of 10^{-5} – 10^{-6} S/cm.

These aluminate polymer single-ionic electrolytes, with improved ionic conductivity, made it possible to construct batteries of type (1) or (2) without significant polarization. In this article, the desirable properties of single-ionic conductors in the lithium battery are demonstrated.

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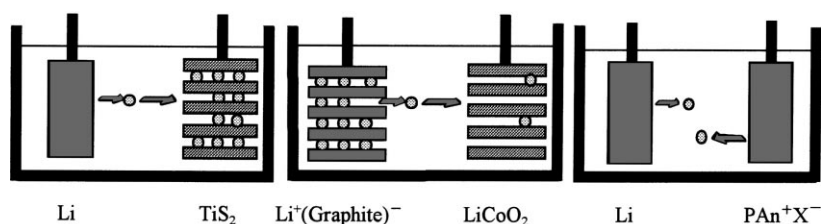


Fig. 1. Lithium batteries; (1) lithium battery (Li/electrolyte/TiS₂), (2) lithium ion battery (graphite-Li/electrolyte/ LiCoO₂), (3) lithium polymer battery (Li/electrolyte/poly(aniline)⁺X⁻).

2. Experimental

2.1. Materials

LiBF₄ (Hashimoto Kasei, battery-grade), HBF₄ (Kishida Chemicals) and poly(vinylidene fluoride) (PVDF; Aldrich) were used as received. Ethylene carbonate, propylene carbonate, aniline and *N*-methylpyrrolidone (Tokyo Kasei) were purified by distillation. Reagent grade LiClO₄ (Wako Pure Chemicals) and acetylene black (AB; Denkikagaku Kogyo) were dried in vacuo at 60°C for a day. TiS₂ (Aldrich) was purified by evaporating excess sulfur in vacuo until the designated stoichiometry was obtained.

2.2. Preparation of poly(aniline)⁺BF₄⁻

Poly(aniline)⁺BF₄⁻ film was prepared on cathode collectors by galvanostatic oxidation polymerization with a Hokuto Denko HA501G potentiogalvanostat at 2 mA/cm² in 1 M aniline + 1 M HBF₄ aqueous solution. Stainless steel and Ni foils were employed as working and counter electrodes. The poly(aniline)⁺BF₄⁻ film on the working electrode was transferred to 1 M HBF₄/LiBF₄ aqueous electrolyte solution, cycled in-between +0.5 and -0.5 V versus SCE at 100 mV/s many times to exclude oligomeric impurities then oxidized at +0.5 V until equilibrated, and immersed in and thoroughly washed with pure water. The film was dried in vacuo at 40°C before use.

2.3. Electrolyte preparation

The aluminate polymer complex (Fig. 2) was prepared according to the previous report [8] in prepurified dimethoxyethane (DME) by the reaction between 1 mol of LiAlH₄, 2 mol of triethylene glycol monomethylether as side chain

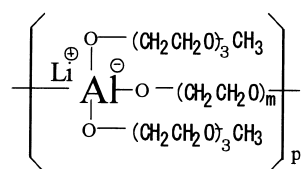


Fig. 2. Aluminate polymer complexes. The average value of *m* is 8.7 for P400.

and 1 mol of poly(ethylene glycol) (MW_{av}=400) as main chain and the resulting aluminate polymer complex was isolated by solvent evaporation and it will be abbreviated as P400. LiBF₄ and LiClO₄ were mixed with P400 in DME and stirred for 2 h at room temperature, then at 70°C for 1 h, and evaporated to dryness in vacuo.

2.4. Cell preparation and measurements

The electrolyte was fabricated into thin films, typically 10 mm diameter × 0.1 mm thickness, sandwiched between stainless steel or metallic lithium electrodes. The ac or both ac and dc conductivity measurements were carried out. The frequency-dependent impedance was measured with a Solartron 1250 frequency response analyzer/1286 potentiostat (10⁻² Hz to 65 kHz) or a Hewlett-Packard HP 4194A impedance/gain-phase analyzer (100 Hz to 40 MHz). The time dependence of dc current was measured at room temperature under an applied voltage of 10.0 mV or 1 V with lithium electrodes using a Hokuto Denko HA501G potentiogalvanostat.

Finely ground TiS₂ powder with 0.5–2 μm diameter was mixed by stirrer with each 10 wt.% of AB and PVDF as binder in *N*-methylpyrrolidone for 3 h, and the mixture was cast on a Ni foil. Thin film lithium secondary batteries were fabricated into 5.5 cm × 4.5 cm × 0.02 cm (thick) cells with a lithium foil (anode; typically 25 μm thick), aluminate polymer complex (solid electrolyte; ca. 50 μm thick) and TiS₂ composite (cathode; ca. 25 μm thick). The charge-discharge property was evaluated by a Hokuto Denko HJ-101SM6 charge/discharge unit.

All experiments including solvent purification, syntheses, cell construction and measurements, hereafter, were conducted under dry argon atmosphere (residual oxygen and water less than 10⁻³ and 0.1 ppm, respectively) in a vacuum-type dry box at room temperature, ca. 22 ± 3°C.

3. Results and discussion

The single-ion nature of aluminate or thioaluminate polyelectrolytes has been confirmed in the previous work [8] and the aluminate type solid electrolyte, P400 (see Fig. 2 and Section 2 for structure), was employed in the cell. Ionic conductors obtained by hybridizing inorganic lithium salts

and P400 may give both anion and cation conductivity. We designated the following three types of solid electrolytes for the cells constructed in the present research:

- (A) $t_{\text{Li}^+} = 1$ and $t_{\text{x}^-} = 0$; P400,
- (B) $t_{\text{Li}^+} = t_{\text{x}^-} = 0.5$; P400 + 2% LiBF₄,
- (C) $t_{\text{Li}^+} \ll t_{\text{x}^-}$; P400 + 5% LiClO₄

The transport number of types (A)–(C) was estimated from the ac–dc steady-state method [10,11] according to Eq. (1),

$$t_+ = \frac{I^S(\Delta V - I^0 R_1^0)}{I^0(\Delta V - I^S R_1^S)} \quad (1)$$

where ΔV is the potential applied across the cell; I^0 and I^S are the initial and steady-state current, and R_1^0 and R_1^S , are the initial and steady-state resistance, respectively. The t_{Li^+} values of electrolyte (A), (B) and (C) were observed to be 0.995, 0.64 and 0.01, respectively. These differences can be seen in Fig. 3. Due to the single-ionic nature the dc-conductivity of P400 measured in the (Li/P400/Li) cell exhibited minimal decay upon prolonged application of the potential, but that of P400+5% LiClO₄ decayed significantly (over 2 orders of magnitude).

3.1. Battery properties

The test cells of (Li/electrolyte/TiS₂) were fabricated with 4.5 cm × 5.5 cm area (effective electrode area = 10 cm²) and the 0.2–0.3 mm thick. The plastic housing was 0.1 mm thick and therefore the actual cell thickness was as thin as 0.1–0.2 mm (Fig. 4). An open circuit voltage as high as 2.8 V was achieved. Since the majority of cell impedance is attributed to the high electrolyte impedance, the energy density (current) for the discharge process was estimated of electrolyte by impedance measurements in separated experiments.

The discharge curves of the first cycle for three electrolytes at a cutoff voltage of 1.5 V is shown in Fig. 5. The

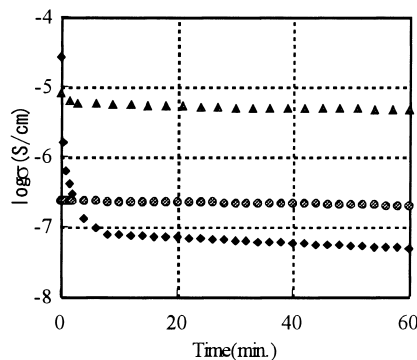


Fig. 3. Time dependence of dc conductivity at 1 V measured with (Li/electrolyte/Li) constitution; (○) P400, (△) P400 + 2% LiBF₄, (◇) P400 + 5% LiClO₄.



Fig. 4. Thin film lithium battery; (Li/P400/TiS₂).

properties of each cell composed of electrolyte systems (A)–(C) described above are as follows:

- (A) $t_{\text{Li}^+} = 1$, $t_{\text{x}^-} = 0$ electrolyte cell, capacity = about 146 mA h/g with a distinct plateau potential of about 2.2 V;
- (B) $t_{\text{Li}^+} = t_{\text{x}^-} = 0.5$ electrolyte cell, capacity = 26 mA h/g without a clear plateau;
- (C) $t_{\text{Li}^+} \ll t_{\text{x}^-}$ electrolyte cell, capacity = 6 mA h/g with no plateau.

In cell (A), the single-ionic nature of electrolyte minimizes the polarization during discharge, the best cell performance was established. In the cells (B) and (C), the mobile anions are gradually concentrated near the anode causing polarization and the discharge process displays a very small cell capacity. In the cell (C), severe polarization diminished the capacity to only 3% of cell (A). Relatively high impedance of P400 caused an overpotential in the discharging and charging processes as shown in Fig. 6, but one can repeat the cycle for more than 100 times with 99% performance.

When the cell was the type shown in Fig. 1(1) or (2), the importance of single-ionic nature of electrolytes was understandable. The remaining cell composition of Fig. 1(3) is uncommon in recent years. When the metallic lithium anode is replaced by graphite-Li, the cell fabrication becomes easy because hazardous and expensive heavy metal sources are not used. To promote the cell reaction of Fig. 1(3), exact

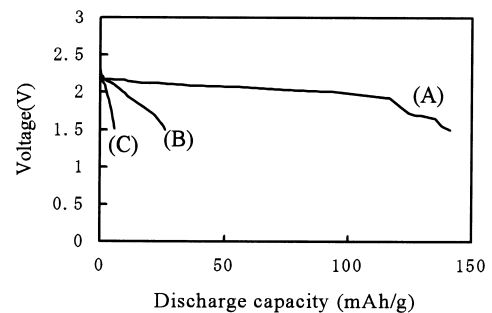


Fig. 5. Discharge property of (Li/electrolyte/TiS₂) battery measured chronoamperometrically at 10 μA/cm²; (A) $t_{\text{Li}^+} = 1$, $t_{\text{x}^-} = 0$ electrolyte (pure P400) cell, (B) $t_{\text{Li}^+} = t_{\text{x}^-}$ electrolyte (P400 + 2% LiBF₄) cell, (C) $t_{\text{Li}^+} \ll t_{\text{x}^-}$ electrolyte (P400 + 5% LiClO₄) cell.

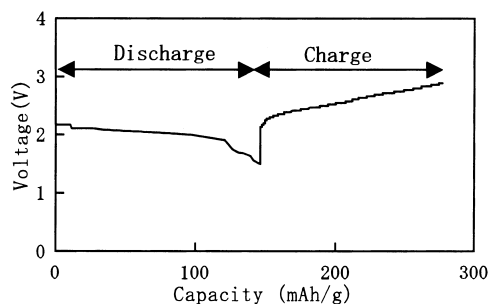


Fig. 6. Charge–discharge property of (Li/P400/TiS₂) battery measured chronoamperometrically at 10 $\mu\text{A}/\text{cm}^2$.

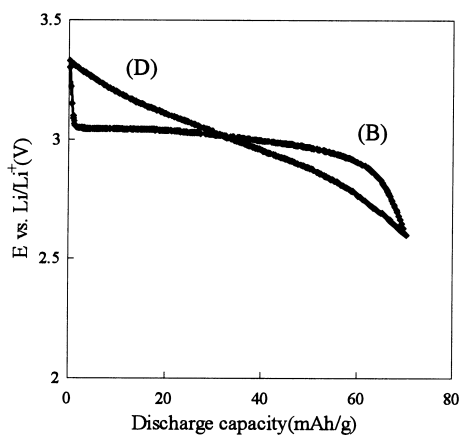


Fig. 7. Discharge property of (Li/electrolyte/poly(aniline)⁺BF₄⁻) battery measured chronoamperometrically at 10 $\mu\text{A}/\text{cm}^2$. Electrolyte (B): $t_{\text{Li}^+}=t_{\text{x}^-}$ -electrolyte (P400+2% LiBF₄), electrolyte (D): 1 M LiBF₄ in propylene carbonate/ethylene carbonate (50/50, v/v).

bi-ionic conductors, $t_{\text{Li}^+}=t_{\text{x}^-}$, are required [9]. In Fig. 7, two discharge curves are compared for (Li/electrolyte/poly(aniline)⁺BF₄⁻) cells where the electrolyte is either ordinary salt solution or solid electrolyte (B). The cell of solid electrolyte (B), where $t_{\text{Li}^+}=t_{\text{x}^-}=0.5$, gave a distinct

discharge plateau with reasonable output voltage. On the other hand, that of the solution-phase electrolyte showed a constantly decreasing discharge curve, because the imbalance of transport numbers, ($t_{\text{x}^-}>t_{\text{Li}^+}$), caused gradual polarization. More detailed studies on the type (3) cell will be provided elsewhere.

4. Conclusion

Thin film lithium batteries composed of aluminate polymer complexes as single-ionic solid electrolytes were fabricated. These batteries showed minimal decay of output voltage upon constant current discharge and their capacity of first cycle was about 146 mA h/g. By contrast a typical bi-ionic conductor of (aluminate polymer complex+5% LiClO₄) hybrid system showed rapid decay of output voltage due to the polarization.

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