

Discharge characteristics of an Li/LiCoO₂ cell with poly(acrylonitrile)-based polymer electrolyte

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Abstract

The electrochemical properties of poly(acrylonitrile) (PAN)-based polymer electrolyte and the discharge characteristics of an Li/LiCoO₂ cell were investigated. The PAN-based polymer electrolyte maintained an ionic conductivity of 1 mS/cm at room temperature, irrespective of storage time. Also, this electrolyte showed high electrochemical stability up to 4.3 V (versus Li⁺/Li). An Li/LiCoO₂ cell battery with this electrolyte has been fabricated and tested. This battery showed good cycling performance. © 1997 Published by Elsevier Science S.A.

Keywords: Discharge; Lithium rechargeable batteries; Polymer electrolytes

1. Introduction

Among the lithium-intercalatable cathodes, LiCoO₂ has been an attractive cathode material because it can be charged and discharged reversibly in the range of high 4 V voltage, and has a high gravimetric energy density [1]. Lithium polymer rechargeable batteries offer many advantages over conventional liquid-based batteries such as safety, light weight, flexible design and relatively low cost.

This paper characterizes the electrochemical properties of the polymer electrolyte and the adding effect of conductive material in the composite cathode on the cycling performance of a lithium polymer battery.

2. Experimental

The composite cathode consisted of LiCoO₂-active material (Cyprus Foote Mineral), Ketjen Black (KB, Mitsubishi Chemical Co.) as a conductor and a polymer electrolyte as a binder. Cathode films were prepared by casting the appropriate ethyl alcohol slurry on an aluminum foil (18 μm thickness) current collector. The polymer electrolyte consisted of a poly(acrylonitrile) (PAN) matrix, LiPF₆ lithium salt, and a mixture of ethylene carbonate and propylene carbonate. The electrolyte film was prepared by casting the viscous polymer solution, with a doctor blade, on the stainless-steel plate. Lithium polymer batteries using lithium foil anode with a

thickness of 125 μm were constructed in a dry argon-filled glove box. The cycle test of this battery was performed in the 3.0–4.3 V range by a galvanostatic method.

3. Results and discussion

PAN-based polymer electrolyte maintained ionic conductivity of 1 mS/cm at room temperature irrespective of storage time, see Figs. 1 and 2. This implies that the liquid electrolyte in the polymer matrix has not lost its electrochemical prop-

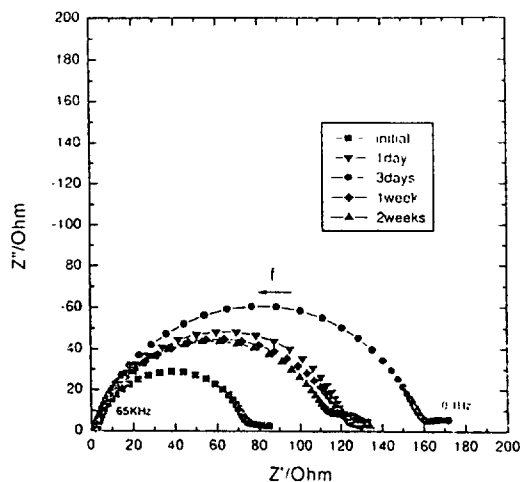


Fig. 1. A.c. impedance spectrum of Li/polymer electrolyte/Li cell vs. storage time at room temperature

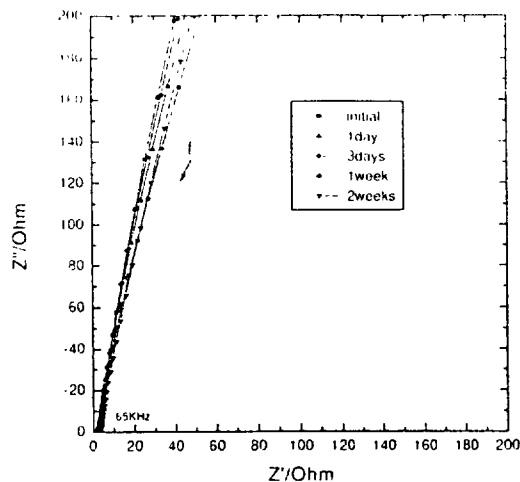


Fig. 2. A.c. impedance spectrum of stainless-steel/polymer electrolyte/stainless-steel cell vs. storage time at room temperature.

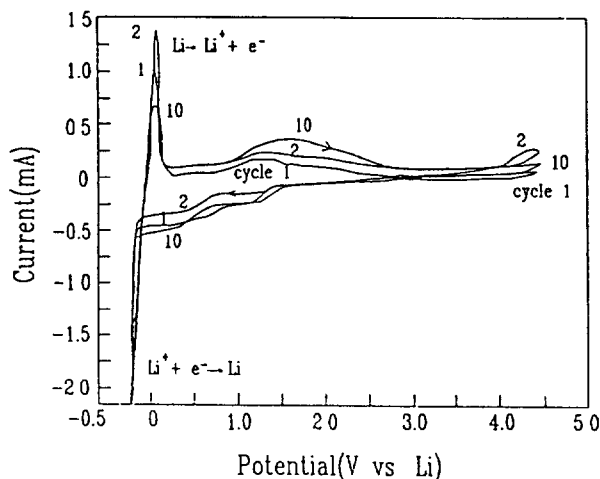


Fig. 3. Cyclic voltammogram of Li/polymer electrolyte/stainless-steel cell; sweep rate 5 mV/s; and electrode area. 2 cm².

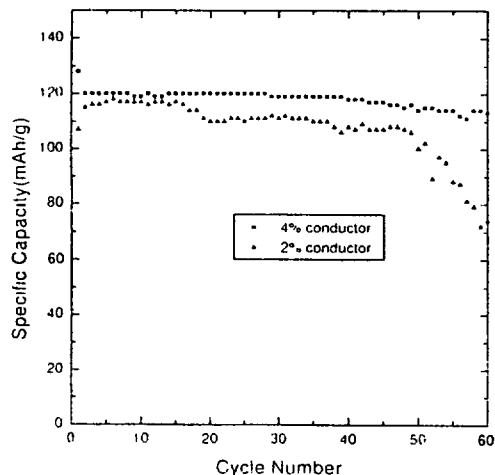


Fig. 4. Cycling performance of Li/polymer electrolyte/LiCoO₂ cell vs. conductive material contents at C/8 rate

erties because of the nonvolatile properties of organic solvent. Fig. 3 showed that this electrolyte was electrochemically stable up to 4.3 V (versus Li⁺/Li). So PAN-based polymer electrolyte showed sufficiently good electrochemical properties to allow safe operation in lithium rechargeable battery systems.

As shown in Fig. 4, the specific capacity value of the composite cathode, containing 2 and 4 wt.% of the conductive material (KB), was similar up to ten cycles. However, the cathode containing 2 wt.% KB exhibited a shorter cycle life. This effect may be associated with the electrical isolation of some active material particles within the composite cathode. Saidi and Barker [2] have reported that composite cathodes based on V₆O₁₃ with a suitable amount of conductive carbon were shown to deliver excellent discharge capacities. As shown in Figs. 5 and 6, the discharge capacities of a battery containing 4 wt.% of the conductive material sustained 125 mAh/g after prolonged cycles at C/8 and C/4 rates and the mean discharge voltage was about 3.9 V but the capacity at

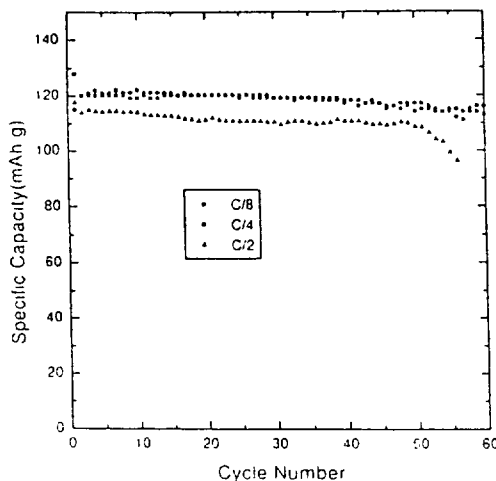


Fig. 5. Cycling performance of Li/polymer electrolyte/LiCoO₂ (4 wt.% KB) cell vs. cycling rate.

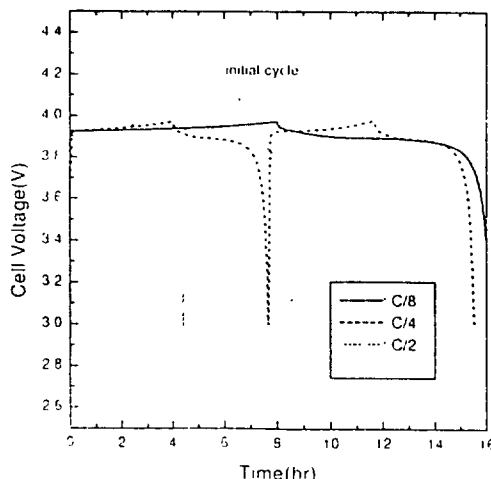


Fig. 6. Voltage profiles of Li/polymer electrolyte/LiCoO₂ (4 wt.% KB) cell vs. cycling rate.

$C/2$ was a little lower and rapidly declined after 50 cycles. It is considered that the poor cycling performance at a high charge/discharge rate was due to the low diffusion rate of the lithium ion in the lattice of the LiCoO_2 solid phase.

4. Conclusions

The PAN-based polymer electrolyte displays electrochemical properties that are sufficient to allow operation in an Li/

LiCoO_2 cell. An LiCoO_2 composite cathode containing 4 wt.% of the conductive material (KB) has high material utilization and good cycling performances compared with cathodes containing 2 wt.% KB.

References

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- [2] M.Y. Saidi and T. Barker, *Solid State Ionics*, 78 (1995) 169.