

Performance of polyaniline positive in a lithium battery*

Yang Lan-sheng**, Shan Zhong-qiang and Liu Ye-dong

Department of Applied Chemistry, Tianjin University, Tianjin 300072 (China)

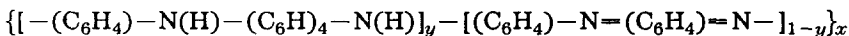
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Abstract

The cyclic voltammetric, open-circuit potential (related to percent. oxidation), stability, and constant current charge/discharge characteristics of a polyaniline positive electrode in a lithium battery system with a non-aqueous electrolyte of 1 M LiClO₄ in propylene carbonate have been determined. It was found that the reversibility of the redox reaction and the cell performance of the polyaniline electrode are both superior to those of other conducting polymers.

Introduction

In recent years, several studies have shown that polyaniline is the most stable conducting polymer and can be used as a cathode material for a lithium rechargeable battery with a non-aqueous electrolyte. Kitani *et al.* [1] first reported the use of polyaniline film for this purpose. The film was synthesized electrochemically using a solution of aniline in aqueous HClO₄. Genies *et al.* [2] later stated that polyaniline, acting as a cathode with a Li/Al anode in an electrolyte of LiClO₄ in propylene carbonate, exhibited good cycling performance and good stability. It was suggested that polyaniline can be described by the general formula:



and can exist in certain oxidation states, e.g., in a completely reduced state 'leuco emeraldine' (where $y=1$); in a 50% oxidized state 'emeraldine base' (where $y=0.5$); and in an emeraldine salt form. It was also found [3–6] that a cathode comprising emeraldine base gave the highest capacity (150 A h kg⁻¹ of emeraldine base) and a coulombic efficiency of 95–100%. The reversibility of polyaniline electrodes in aqueous and solid-state electrolytes has also been reported [7, 8]. Seiko Electronic Components Ltd. [10] was the first to produce a rechargeable polymer lithium battery (Models AL920, AL2016, and AL2032 with nominal capacities of 0.5, 2.0, and 8.0 mA h, respectively).

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**Author to whom correspondence should be addressed.

The present investigation concerns the determination of the electrochemical characteristics of various forms of polyaniline electrode and their performance in a lithium rechargeable battery system using an electrolyte of LiClO_4 in propylene carbonate.

Experimental

The emeraldine salt of polyaniline was synthesized chemically as a powder by oxidative polymerization of aniline in aqueous 1 N HClO_4 with ammonium persulfate at room temperature. A green precipitate formed during the first 2 h of reaction and this was filtered off using a Buchner funnel. The precipitate was washed with 0.5 N HClO_4 until the filtrate became colourless. The precipitate was then dried in a vacuum oven for two days at 80 °C.

The emeraldine salt can be converted to either the emeraldine base form or the leuco emeraldine form by treatment with aqueous ammonia or hydrazine, respectively. Samples of the various polyanilines were subjected to commercial analysis.

Cyclic voltammetric studies were undertaken on a film of polyaniline by evaporating a polyaniline solution onto a platinum foil electrode. Positive electrodes were made by pressing polyaniline powder containing 5 wt.% carbon black, with PTFE as a binder, into a sheet and then pressing the sheet onto a nickel mesh. Cells were constructed in an argon dry box using a microporous polypropylene separator between the polyaniline and lithium electrodes. This assembly was housed in a sealed, steel container. The electrolyte consisted of a solution of 1 M LiClO_4 in propylene carbonate (PC).

Electrochemical characteristics of the cells were determined using an HR-101 B potentiostat/galvanostat and an HR-104 function generator. Voltage/time curves were recorded with an X-Y recorder. All electrode potentials are reported with regard to a lithium reference electrode. All experiments were conducted at room temperature.

Results and discussion

The cyclic voltammogram for a polyaniline electrode in an electrolyte of 1 M LiClO_4 in propylene carbonate is shown in Fig. 1. It is found that the amount of charge passed during the positive-going scan from 2.5 to 4.0 V is almost the same as that for the reverse scan to 2.5 V, despite the fact that there is a difference in the shape of the two voltammetric curves. This result suggests that the redox reaction of a polyaniline electrode in non-aqueous electrolyte is reversible. The reversibility is further demonstrated by the charge and discharge curves for a polyaniline positive in a lithium battery using a non-aqueous electrolyte, see Fig. 2. Each curve was obtained over ~ 10 h at a constant current of 0.3 mA cm^{-2} . The charge curve was

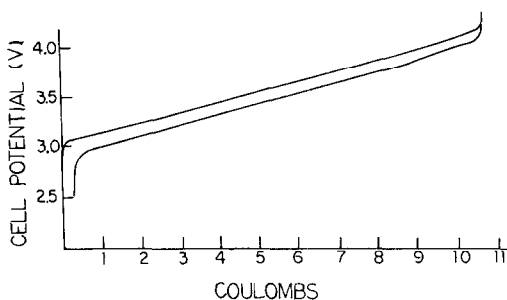
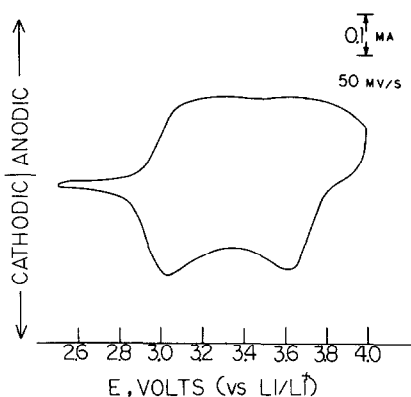


Fig. 1. Cyclic voltammogram of a polyaniline electrode in 1 M LiClO_4/PC electrolyte. Scan rate 50 mV s^{-1} .

Fig. 2. Typical charge/discharge curve for a polyaniline/1 M $\text{LiClO}_4(\text{PC})/\text{Li}$ cell.

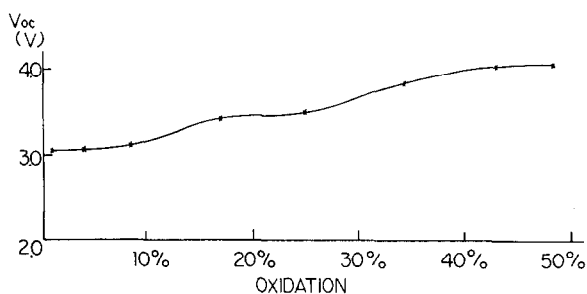


Fig. 3. Relationship between V_{oc} and degree of oxidation of polyaniline in 1 M $\text{LiClO}_4(\text{PC})$.

stopped at 4.20 V because the potential began to rise rapidly; correspondingly, the potential of the discharge curve began to fall rapidly at 3 V. The data clearly show that the discharge of polyaniline positives is almost complete at 2.5 V (98% coulombic capacity). The observed reversibility of the polyaniline electrode reaction in a non-aqueous electrolyte is similar to that found in both aqueous and solid-state electrolytes [7, 8].

The dependence of the potential of a polyaniline electrode (open-circuit voltage, V_{oc}) on the degree of oxidation is given in Fig. 3. The potential rises from 3.0 to 3.9 V as oxidation increases to 50%. This relationship is similar to that of P-doped polyacetylene in an electrolyte of 1 M LiClO_4 in propylene carbonate [9]. The potential of a conducting polymer electrode is only dependent on the degree of oxidation of the polymer, thus differing from that of metal oxide electrodes where the concentration of anions in the electrolyte exerts an influence.

Polyaniline can be oxidized up to 50%: this is greater than that for polyacetylene (oxidation limit = 7%). Therefore, polyaniline used as a positive in a lithium battery can exhibit a greater degree of material utilization.

Polyaniline can be prepared in various forms that display marked differences in performance. The coulombic efficiency of various forms of polyaniline over 10 cycles is shown in Fig. 4. The emeraldine base form yields the highest efficiency, viz., a constant 95%. Furthermore, the molecular weight of the emeraldine base is less than that of the salt form, and thus the corresponding capacity per unit weight is larger.

When discharged at 0.3 mA cm^{-2} , the experimental capacity of a Model 2430 button cell (using polyaniline salt form as the positive material) was found to be about 10 mA h. This result agrees with previous studies [10]. The effective utilization of the emeraldine salt is about 50%.

The change in open-circuit potential of a completely charged cell as a function of standtime is presented in Fig. 5. It can be seen that the potential decreases slowly with time. After 30 days, the potential has fallen from 3.9 to 3.5 V and about 50% of the original charge can be drawn from the cell. The rate of self-discharge during the same period is low, viz., 2% per day; this agrees with other published data [6]. It is concluded that the shelf life of the polyaniline-positive lithium system is the best of the electronic-conducting-polymer types of batteries.

These preliminary results clearly demonstrate the promise offered by polyaniline as a positive material for rechargeable lithium batteries. Its

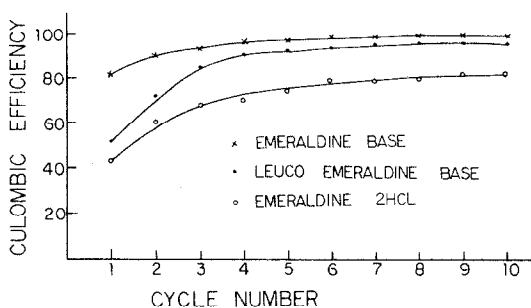


Fig. 4. Coulombic efficiency of various forms of polyaniline.

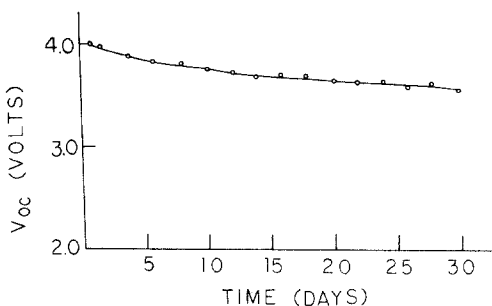


Fig. 5. Open-circuit voltage of completely charged polyaniline/1 M $\text{LiClO}_4(\text{PC})/\text{Li}$ cell as function of stand time.

performance is superior to that of any other conducting polymer reported to date.

References

- 1 A. Kitani, M. Kaya and K. Sasaki, *Abstr. 24th Battery Symp., Osaka, Japan, Nov. 9-14, 1983*.
- 2 E. M. Genies, A. A. Syed and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, 121 (1985) 181.
- 3 A. G. MacDiarmid and L. S. Yang, *170th Meet. Electrochem. Soc., San Diego, CA, U.S.A., Oct. 19-24, 1986*, Ext. Abstr. No. 2.
- 4 A. G. MacDiarmid, L. S. Yang, W. S. Huang and B. D. Humphery, *Synth. Met.*, 18 (1987) 393.
- 5 K. Okabayashi, F. Goto, K. Abe and T. Yoshida, *Synth. Met.*, 18 (1987) 365.
- 6 F. Goto, K. Abe, K. Okabayashi, T. Yoshida and H. Morimoto, *J. Power Sources*, 20 (1987) 243.
- 7 L. S. Yang, Z. Q. Shan and Y. D. Liu, *Ext. Abstr., 7th Int. Conf. Solid State Ionics, Japan, Nov. 5-11, 1989*, pp. 9aA-08.
- 8 L. S. Yang and W. L. Zhang, *Prepr. 3rd China-Japan Joint Symp. Conduction and Photo-conduction in Organic Solids and Related Phenomena, China, May 16-18, 1989*, p. 46.
- 9 R. B. Kaner and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. I*, 80 (1984) 2109.
- 10 *JEC Battery Newsletter*, 6 (1989) 4.