

Design of polyacene-based negative electrode for polymeric gel electrolytes

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Abstract

Composition of polyacene (PAS)-based negative electrode has been optimized to be suitable for rechargeable battery systems with polymeric gel electrolytes. The gel electrolytes consisted of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as a host polymer, a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as a plasticizer, and LiX (X = ClO₄ or (C₂F₅SO₂)₂N) as a carrier salt. Three types of composite PAS electrodes were prepared and their compatibility with the polymeric gel electrolytes was examined. A half cell assembled with the composite PAS electrode containing proper amounts of polymeric gel and the electrolyte film with the same gel composition showed good cycling characteristics. The gel composition containing 1.0 mol dm⁻³ (M) Li(C₂F₅SO₂)₂N/(EC + DEC) gave discharge capacity of about 600 Ah kg⁻¹ (with respect to the mass of PAS) with high rechargeability.

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1. Introduction

Since a lithium (Li)-ion battery was first introduced into portable electronic devices in the early 1990s, a number of carbon materials have been proposed as the negative electrodes of the batteries with high energy density [1,2]. The present Li-ion batteries mainly use artificial or natural graphite whose theoretical capacity is 372 Ah kg⁻¹ (C₆Li). Some systems have employed so-called hard carbon with very low atomic ratio of H/C, which can store more lithium than graphite. Polyacene (PAS), a peculiar form of the hard carbon prepared by pyrolysing phenolic resin [3], has an essentially amorphous structure. It contains pores of different scales so that it can be doped with large amounts of Li [4–6]. Yata et al. have shown for the first time [7] that PAS has much higher capacity than the graphite, i.e. up to 1100 Ah kg⁻¹, the value of which is equivalent to the composition of

C₂Li, being approximately three times higher than the graphite-based electrodes [5]. This is a marked advantage for fabricating high-capacity anode of Li ion batteries with high energy density. We have investigated the influences of the electrolyte composition on the battery performances of the PAS electrode [8,9]. The experimental results of charge and discharge cycling and AC impedance analysis demonstrated that the reversible capacity of 600 Ah kg⁻¹ has been established in the electrolyte composition of ethylene carbonate (EC) mixed with diethyl carbonate (DEC) dissolving Li(C₂F₅SO₂)₂N as the electrolytic salt.

Recently, polymeric gel electrolytes have widely been studied from the viewpoints of the safety and reliability of the battery system. Those gel systems consist of polymer matrices swollen with organic electrolyte solutions, and are adopted to the practical Li ion batteries [10]. We have also investigated the polymeric electrolytes composed of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) matrix swollen with organic electrolyte solution for PAS electrode. The basic properties of PVdF-HFP-based gel

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electrolytes and their compatibility to the carbon anode have so far been reported [11–14]. However, little has been published on the combination of hard carbon anodes and PVdF-HFP-based gel electrolytes. The preliminary results on the basic properties of gel electrolytes and the charge–discharge cycling tests have proved that the optimized composition of PVdF-HFP-base gel electrolyte can deduce the best performance of the PAS electrode [15].

In this work, we have further examined the electrode composition that enables PAS-based electrode having high capacity and cycleability in solid gel electrolytes. That is, the purpose of the present work is to optimize the electrode composition for obtaining higher performance of the PAS electrode using polymeric gel electrolytes.

2. Experimental

The organic solvent, ethylene carbonate (EC) and diethyl carbonate (DEC) (Kishida Chemical; Battery grade), were used as received. The electrolytic salts, anhydrous LiClO_4 (Wako Pure Chemical) and $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ (Ryoko Chemical), were dried under a vacuum at 120°C for 24 h or longer before use. Polyacene (PAS), developed by Kanebo, was provided as a composite sheet electrode pressed on a Cu foil substrate and as powder with a particle size of ca. $4\ \mu\text{m}$. PAS sheet electrode was dried under a vacuum at 120°C over 8 h before use. Activated carbon powder made from coconut-shell with specific surface area of ca. $1700\ \text{m}^2\ \text{g}^{-1}$ was used after proper pretreatments.

The polymeric gel electrolytes based on PVdF-HFP were prepared by the same way as described previously [15].

Three types of PAS electrodes were prepared in this work. The first one is a mixture of PAS as the active material and PVdF as the binder, which is referred to “Conventional electrode” or “Type A electrode” hereinafter. The second one consisted of the active mass PAS, the gel former PVdF-HFP and the ionic conductor $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ (or LiClO_4) dissolved in EC + DEC, in a mass ratio of 4:1:8, which is denoted as “Advanced electrode” or “Type B electrode”. This type of electrode was prepared as follows: Viscous slurries was made of PAS, PVdF-HFP, $1.0\ \text{mol}\ \text{dm}^{-3}$ (M) $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ (or

LiClO_4)/(EC + DEC) and 1-methylpyrrolidine-2-on (NMP) solvent. Each component was well-mixed (over 24 h) and then coated onto a Cu foil current collector ($8\ \text{mm} \times 8\ \text{mm}$, $200\ \mu\text{m}$ thick). After that, it was dried under a reduced pressure (ca. 50 kPa) at 70°C for 6 h. The third type (Type C) of PAS electrode consisted of PAS mixed with proper amounts of the activated carbon (1:1 by mass), PVdF-HFP and $1.0\ \text{M}$ $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ /(EC + DEC), which is donated as “Hybrid electrode” in this paper.

The charge and discharge characteristics of three kinds of PAS electrodes were investigated using an Li/PAS half cell under conditions of constant current/constant potential (cc-cv) charge and constant current (cc) discharge, typically with a current density of $1.0\ \text{A}\ \text{m}^{-2}$. The charging process was controlled by the designated capacity (first cycle: $1000\ \text{Ah}\ \text{kg}^{-1}$, second cycle and after: $600\ \text{Ah}\ \text{kg}^{-1}$).

3. Results and discussion

The anodic characteristics of the Conventional (Type A) electrode consisting of PAS and PVdF binder were investigated in the polymeric gel electrolytes with different composition. We have proved that the optimized composition of PVdF-HFP-base gel electrolyte can extract the best performance of the PAS electrode [15]. That is, the Type A electrode showed high discharge capacity in the polymeric gel electrolyte using $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ as the electrolytic salt, PVdF-HFP/ $1.0\ \text{M}$ $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ /(EC + DEC). The capacity obtained at the initial cycle was almost the same as that reported in the solution electrolyte. With respect to the cycleability, however, the discharge capacity was markedly decreased with repeated cycles [15]. This capacity fading with the cycle was supposed to be due to the inhibited mass transfer between the PAS electrode and the gel electrolyte. Thus, in the present work, we have optimized the composition of the PAS electrode. The Advanced (Type B) electrode was prepared by blending PAS, PVdF-HFP and the Li salt dissolved in the organic solvent, in which both the electron and ion transport occur effectively through optimized interface between the electrode active mass (PAS) and the ion-conductive phase (Li salt with the organic solvent).

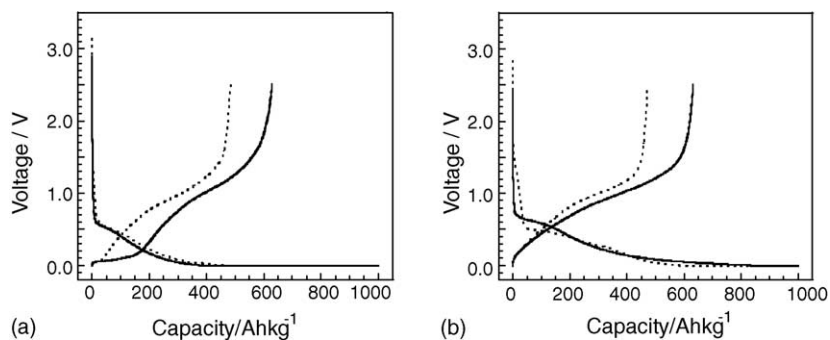


Fig. 1. Charge–discharge curves for PAS electrodes using EC + DEC gel electrolytes at first cycle. (a) Type A (Conventional) electrode and (b) Type B (Advanced) electrode. (---) LiClO_4 ; (—) $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$.

Fig. 1 shows the first charge and discharge performances of the Type B electrode in the polymeric gel using EC + DEC component compared with that of the Type A electrode. The charge and discharge curves for the Type B electrode (Fig. 1(b)) show similar profile to that obtained in the organic electrolyte solutions previously studied [8,9]. The potential plateau corresponding to the deposition/dissolution of metallic lithium on/from the PAS electrode is observed for the Type A electrode at around 0 V as shown in Fig. 1(a), while the Type B electrode does not show such potential plateau due to the metallic Li deposition. This suggests that the interface between the active mass and the ion-transport phase was improved in the Type B electrode, and then the diffusion of Li^+ ion in the Type B electrode occurs more easily than the Type A electrode. Both electrodes showed large irreversible capacity, which is typically observed for hard carbon anodes prepared at low temperature as below 1000°C [16]. This type of the irreversible capacity is considered to be caused by irreversible reduction of functional groups of the carbon material, or irreversible strong adsorption of Li on a certain site within the carbon material. Actually, as PAS electrode used in this study was prepared by pyrolysis of phenolic resin at $500\text{--}700^\circ\text{C}$, the large irreversible capacity in the first cycle should be due to such irreversible reactions as observed for typical hard carbon materials.

The variation in the discharge capacity of the Type B electrode during the cycle in the gel electrolytes is shown in Fig. 2, compared with that obtained for the Type A electrode. The cycle performance of the Type B electrode was much improved although the first discharge capacity of the Type B electrode was almost the same as that of the Type A electrode. With respect to the sort of the salt in the Type B electrode, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ gave better cycle performance than LiClO_4 . These results reveal that the interface between the electrode and the polymeric gel electrolyte was improved by designing the electrode structure appropriately. Cycling performances as high as those obtained in solution electrolytes were realized for the PAS electrode in the present gel system by choosing suitable electrolyte composition.

Next the rate capability of the PAS electrode in the gel electrolyte system has been examined. Effects of the addition of the activated carbon powder into the Type B electrode

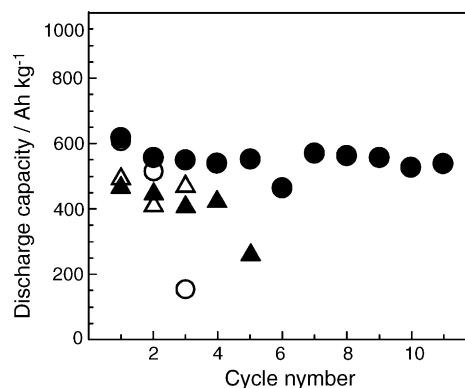


Fig. 2. Discharge capacity of PAS electrodes using EC+DEC gel electrolytes. (●) Type B electrode ($\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$), (○) Type A electrode ($\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$), (▲) Type B electrode (LiClO_4), (△) Type A electrode (LiClO_4).

were investigated. Fig. 3 shows the charge–discharge curves for the Hybrid (Type C) electrode using $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}/(\text{EC} + \text{DEC})$ gel electrolyte (Fig. 3(b)), compared with those for the Type B electrode (Fig. 3(a)). The charge–discharge profile of the Type C electrode showed different characteristics from the Type B electrode, which include both characteristics of the activated carbon and PAS. That is, the charge–discharge profiles of the Type C electrode showed rather linear potential variation, being characteristics to the profile of the capacitor electrode, where the ions are physically adsorbed on and desorbed from the high surface area of the activated carbon. Thus, it can be regarded as the linear behavior of the initial discharge profile being due to the activated carbon and the discharge profile over 1.3 V being due to the Faradic process of PAS. The discharge capacity per mass of the active materials (PAS) was gradually decreased with the repeated cycle for the Type B electrode as shown in Fig. 3(a). On the other hand, the discharge capacity (Ah kg^{-1}) of PAS and the activated carbon) was increased with the repeated cycle for the Type C electrode, as shown in Fig. 3(b). Large irreversible capacity was still observed in Fig. 3, which would be caused by the same reason as described previously.

The rate capability of PAS electrode was evaluated by the dependence of discharge capacity on the current density. The

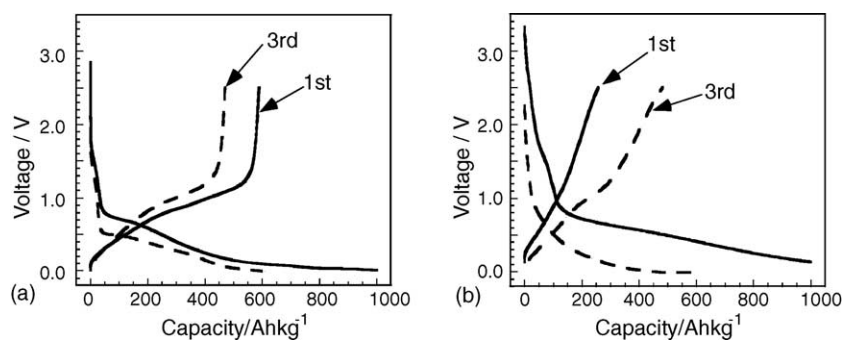


Fig. 3. Charge–discharge curves for PAS electrode using $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}/(\text{EC} + \text{DEC})$ gel electrolyte. Discharge current density: 1.0 A m^{-2} . (a) Type B electrode and (b) Type C electrode.

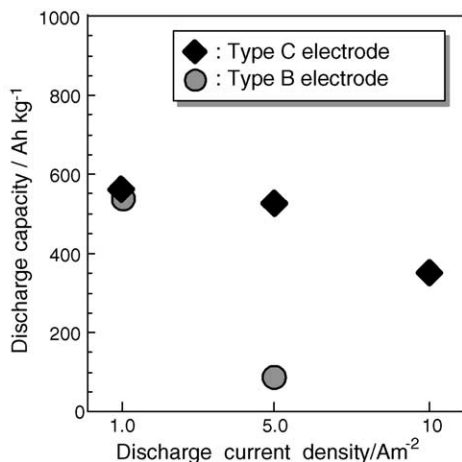


Fig. 4. Rate capability of PAS electrodes at fifth cycles.

Li/PAS half cell was charged under constant current/constant potential with controlled capacity, whose condition is described in Section 2. The cell was discharged under the constant current conditions (1.0, 5.0 and 10 A m⁻², respectively). Fig. 4 shows comparison of the rate capability of the Type B and the Type C electrodes at their fifth cycles. The discharge capacity for the Type B electrode was significantly decreased with the increase in the applied current density. However, for the Type C electrode, the discharge capacity of about 400 Ah kg⁻¹ was kept even the applied current density was increased to 10 A m⁻². Addition of the activated carbon powder in the Type B electrode showed a positive effect on the rate performance of the PAS electrode in the present gel electrolyte system.

4. Conclusions

The electrode composition that should be suitable for the PAS-battery system with a polymeric gel electrolyte has been examined. The Type B (Advanced) electrode consisting of the active mass PAS, the gel former PVdF-HFP and the ionic conductor Li(C₂F₅SO₂)₂N dissolved in EC+DEC showed similar charge–discharge performances as those in the organic electrolyte solutions.

The Type C electrode named “Hybrid electrode” that consisted of PAS and activated carbon pow-

der (1:1 by mass) mixed with PVdF-HFP and 1.0M Li(C₂F₅SO₂)₂N/(EC+DEC) showed the good rate capability. The addition of activated carbon powder in the Type B showed a positive effect on the rate performance in the present gel electrolyte system.

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References

- [1] M.B. Armand, in: D.W. Murphy, J. Broadhead, B.C. Steele (Eds.), *Materials for Advanced Batteries*, Plenum Press, New York, NY, 1980, p. 145.
- [2] D. Guymard, J.M. Tarascon, *J. Electrochem. Soc.* 139 (1992) 937.
- [3] K. Tanaka, K. Ohzeki, T. Yamabe, S. Yata, *Synth. Met.* 9 (1984) 41.
- [4] H. Ago, K. Tanaka, T. Yamabe, T. Miyoshi, K. Takegoshi, T. Terao, S. Yata, Y. Hato, S. Nagura, N. Ando, *Carbon* 35 (1997) 1781.
- [5] S. Yata, Y. Hato, H. Kinoshita, N. Ando, A. Anekawa, T. Hashimoto, M. Yamaguchi, K. Tanaka, T. Yamabe, *Synth. Met.* 73 (1995) 273.
- [6] N. Ando, Y. Hato, T. Yoshii, Y. Natsume, A. Ito, K. Tanaka, *Thin Solid Films* 393 (2001) 177.
- [7] S. Yata, H. Kinoshita, M. Komori, N. Ando, T. Kashiwamura, T. Harada, K. Tanaka, T. Yamabe, in: *Proceedings Symposium on New Sealed Rechargeable Batteries and Supercapacitor*, Honolulu, Hawaii, USA, 16–21 May 1993, *Proceedings of the Electrochemical Society*, vol. 92–93, Electrochemical Society, Pennington, NJ, p. 502.
- [8] M. Ishikawa, T. Fukushima, S. Momota, M. Morita, Y. Matsuda, A. Anekawa, Y. Hato, S. Yata, *The 37th Battery Symposium in Japan*, Abstract (2A28), 1996, p. 165.
- [9] S. Momota, M. Ishikawa, M. Morita, M. Yamaguchi, Y. Hato, *The 39th Battery Symposium in Japan*, Abstract (3D13), 1998, p. 445.
- [10] B. Scrosati, *Advances in Lithium-Ion Batteries*, Kluwer Academic/Plenum Publications, New York, 2002, Chapter 8, p. 251.
- [11] L. Christie, A.M. Christie, C.A. Vincent, *J. Power Sources* 81–82 (1999) 378.
- [12] J. Chojnacka, J.L. Acosta, E. Morales, *J. Power Sources* 97–98 (2001) 819.
- [13] J.Y. Song, H.H. Lee, Y.Y. Wang, C.C. Wan, *J. Power Sources* 111 (2002) 255.
- [14] L. Fan, Z. Dang, C.-W. Nan, M. Li, *Electrochim. Acta* 48 (2002) 205.
- [15] N. Yoshimoto, A. Okamoto, M. Ishikawa, M. Morita, N. Ando, Y. Hato, *Electrochemistry* 71 (2003) 1049.
- [16] K.R. Zavadil, N.R. Armstrong, *J. Electrochem. Soc.* 137 (1990) 2371.