

## Lithium-ion rechargeable cells with polyacenic semiconductor (PAS) and LiCoO<sub>2</sub> electrodes

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### Abstract

Polyacenic semiconductor (PAS), heat-treated at 700 °C, has a lithium intercalation capacity as high as 438 mAh g<sup>-1</sup> which is higher than the theoretical capacity of 372 mAh g<sup>-1</sup> for graphite. The electrochemical behaviour of PAS is examined by studying Li/PAS and Li/graphite cells. In a PAS or graphite anode, three reactions are distinguished: (i) reaction of lithium with the Teflon binder; (ii) decomposition of electrolyte, and (iii) intercalation of Li<sup>+</sup> ions. Two laboratory cells with liquid organic electrolyte or polymer electrolyte and PAS as the anode demonstrate that PAS is a promising anode material for lithium-ion batteries.

**Keywords:** Lithium-ion batteries; Rechargeable lithium cells; Polyacenic semiconductor; Lithium; Electrodes

### 1. Introduction

In recent years, carbon-based materials have been studied extensively as anodes in 'lithium-ion' batteries [1,2]. It should be noted that the energy densities of lithium-ion batteries are much lower than those of lithium batteries due to the limitation of lithium intercalation into graphite. It is well known that the highest intercalation capacity of the first stage, lithium/intercalation graphite compound is 372 mAh g<sup>-1</sup>. This capacity value cannot, however, be obtained in real battery systems due to dynamic reasons. One of the key problems in increasing the energy density of lithium-ion batteries is to find a new anode with a higher intercalation capacity. Recently, we have found [3] that polyacenic semiconductor (PAS) heat-treated at 700 °C possesses a reversible lithium intercalation capacity of 438 mAh g<sup>-1</sup>. This intercalation capacity is much higher than that of first-stage, lithium/graphite intercalation compound. Another obstacle that has to be overcome for improving energy density of lithium-ion batteries is the capacity loss during the first charge process. It has been reported that this capacity loss is more than 50% [4,5]. This phenomenon has been attributed [6] to the reduction of the electrolyte to form an electronically insulating layer on the carbon electrode surface metallic lithium anode in the case of lithium batteries. Some efforts have been made [6,7] to investigate the discharge process and to improve the

performance of lithium-ion batteries. But to date, the reactions that occur in the carbon electrode in lithium-ion batteries during the first charge process are still not fully understood. Recently, we found [8] that the reaction of lithium with binders (Teflon) in the carbon electrode could consume a certain amount of lithium, in addition to causing electrolyte decomposition on the carbon surface.

This paper presents the results of a study on the electrochemical properties of polyacenic semiconductor (PAS) in an lithium-ion battery anode, and its application as the anode in lithium-ion batteries.

### 2. Experimental

PAS was obtained by pyrolyzing phenol-formaldehyde resin under a nitrogen atmosphere at various temperatures with a temperature rise rate of 10 °C h<sup>-1</sup> [9]. The product was ground into powder and mixed with 15 wt.% Teflon powder to form a pellet electrode of 10 mm diameter and 0.1 mm thickness. For impedance measurements, a three-electrode cell was constructed with lithium as the reference and counter electrodes, and the PAS pellet as the working electrode. Two-electrode Li/PAS cells were constructed to investigate the capacity change of PAS during cycling. Comparative tests were performed on Li/graphite cells that

were made using the same procedure for Li/PAS cells, exception for 32.6 wt.% Teflon binder in the impedance-measurement cell. For all cells, the electrolyte was 1 M  $\text{LiPF}_6\text{-EC-DEC}$  (1:1 volume ratio). The separator was Cellgard 2400 polypropylene thin film.

Two laboratory cells were constructed to demonstrate the possibility of PAS as anode material. For cell (A), the electrolyte was 1 M  $\text{LiPF}_6\text{-EC-DEC}$  (1:1 at volume ratio). While for cell (B) the electrolyte was  $\text{LiClO}_4\text{-PAN-EC-BL}$  (5:20:35:40 weight ratio). This latter electrolyte was prepared by dissolving PAN in an appropriate amount of EC+BL and  $\text{LiClO}_4$  at 110 °C then casting to form a film. (Note: EC, ethylene carbonate; DEC, diethyl carbonate; PAN, polyacrylonitrile, and BL, 1,4-butyrolactone.)

The Teflon content in the PAS electrode is 5 wt.%. All cells were constructed in a dry box filled with argon. Measurements of the charge/discharge characteristics of the cells were carried out at room temperature by using a potentiostat/galvanostat with a function generator and an x-y recorder.

Impedance spectra were recorded with a 4192A LF impedance analyser.

### 3. Results and discussion

The electrochemical capacities of several carbon materials are shown in Fig. 1. The capacity of PAS is much higher than that of graphite or graphitized carbon such as coke.

The lithium intercalation capacity of PAS as a function of heat-treatment temperature (HTT) is given in Fig. 2. The capacity increases with rise in the HTT and reaches a maximum value of 438  $\text{mAh g}^{-1}$  when the HTT is about 700 °C. Thereafter, the capacity decreases [10] with further increase in HTT.

Representative cycling results for the Li/PAS and Li/graphite cells are presented in Fig. 3. After about 12 cycles, the capacity reaches a steady value of  $\sim 438 \text{mAh g}^{-1}$  for PAS and  $\sim 245 \text{mAh g}^{-1}$  for graphite. It is obvious that large

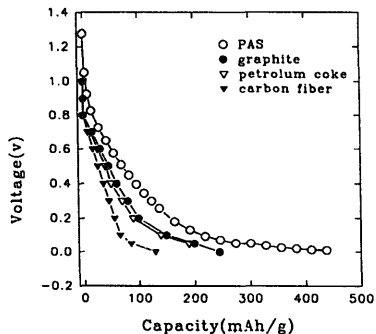


Fig. 1. Discharge capacity of several carbon materials.

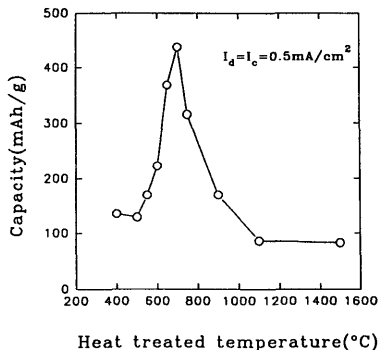


Fig. 2. Lithium intercalation capacity of PAS as function of heat-treatment temperature.

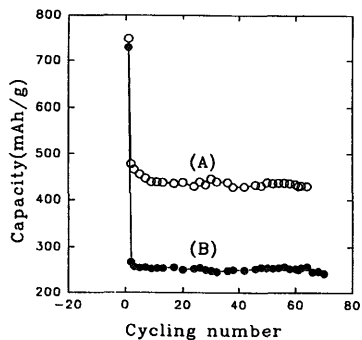


Fig. 3. Discharge capacities of (A) Li/PAS cell and (B) Li/graphite cell as function of cycling number.

capacity losses in the first discharge process are observed for both Li/PAS and Li/graphite cells. The reversible intercalation capacity of PAS is much higher, however, than that of graphite.

The open-circuit voltage (equilibrium values) of the cells as a function of discharge capacity per gram of PAS or graphite are shown in Fig. 4. The two curves are very similar and each can be divided into three regions. In the case of the Li/PAS cell, region I is higher than 1.6 V; region II is in between 1.6 and 0.4 V, and region III is in between 0.4 and 0.0 V. For the Li/graphite cell, by contrast, region I is higher than 2.0 V, region II is between 2.0 and 0.2 V, and region III is between 0.2 and 0.0 V. In region I, lithium intercalation into the graphite layer does not occur, it just reacts with the binder (Teflon) [9].

These results have been supported by X-ray diffraction analysis [8]. The layer spacing  $d_{002}$  of graphite as a function of open-circuit voltage (OCV) for Li/graphite cell is shown

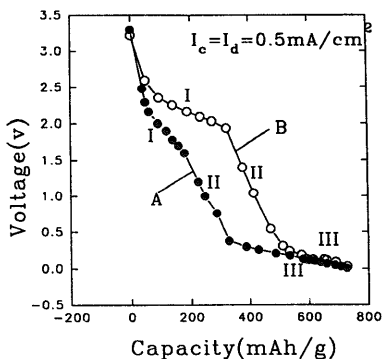


Fig. 4. Open-circuit voltage as a function of discharge capacity of (A) Li/PAS and (B) Li/graphite cells.

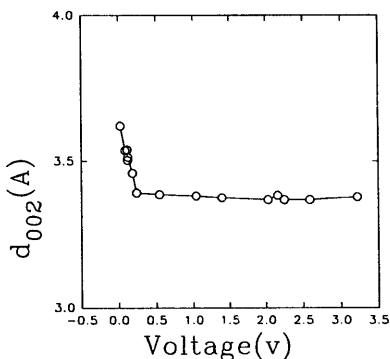


Fig. 5. Layer spacing ( $d_{002}$ ) of graphite as a function of open-circuit voltage of Li/graphite cell.

In Fig. 5. The data reveal that three different processes occur in the carbon electrode during the first discharge process of the Li/graphite cell. In region I, there is virtually no change in  $d_{002}$  during the lithium-transfer process into the carbon electrode, as shown in Fig. 5. In region II, the  $d_{002}$  value increases slightly and the OCV decreases quickly when more lithium is transferred into the graphite electrode. The capacity loss in this region is probably caused by decomposition of the electrolyte. As a result, an electronic insulating layer is formed on the carbon surface (PAS or graphite). The remaining lithium is intercalated into the graphite layer and results in a small increase in the layer spacing. The intercalation reaction of lithium into the graphite layer occurs mainly in region III, as indicated by the rapid increase of  $d_{002}$ . Similarly, the lithium intercalation into PAS takes place predominantly below 0.4 V.

In order to confirm the reaction of lithium with the binder (Teflon) in the Li/PAS cell, a further experiment was performed. By mixing PAS and binder (Teflon) at a weight ratio of 80:20, three pellets were prepared (each weighed 12 mg). Each pellet was used in a 2N Li/1 M  $\text{LiPF}_6\text{-EC-DEC}$ /PAS cell; they are numbered A, B, and C. The OCV of each of these cells is around 3.3 V. The cells were then cycled at a constant current density of  $0.2 \text{ mA cm}^{-2}$ , between 3.3 and 0.0 V. After cycling 1, 5, and 10 times for cells A, B, and C, respectively, the PAS electrodes were removed from the cells, and ground and washed with distilled water (20 ml in total for each cell). The solutions corresponding to the cells were named samples (a), (b), and (c).

The concentration of the  $\text{F}^-$  ions in the solution was measured with a fluorine ion-selective electrode. The  $\text{F}^-$  concentration in the solution was: (a)  $9.9 \times 10^{-4} \text{ M}$ ; (b)  $1.104 \times 10^{-3} \text{ M}$ , and (c)  $1.17 \times 10^{-3} \text{ M}$ . The corresponding  $\text{F}^-$  content in the electrode was: (a)  $1.96 \times 10^{-5} \text{ mol}$ ; (b)  $2.208 \times 10^{-5} \text{ mol}$ ; (c)  $2.34 \times 10^{-5} \text{ mol}$ , respectively. Therefore, the F content in (c) was almost equal to the F content in 2.4 mg of Teflon. That is, after 10 cycles, almost all the Teflon had reacted with lithium. The reaction may be represented as:



This phenomenon indicates that the reaction of lithium with Teflon is not finished in the first discharge process, but will last for about 10 cycles. As a result, the discharge capacity will decrease slightly with cycling, as shown in Fig. 3. From the above analysis, it can be seen that the capacity losses during the first discharge process for Li/PAS and Li/graphite cells are caused by both the lithium reaction with Teflon binder and the decomposition of electrolyte.

In order to obtain more information on the large capacity loss in the first discharge process for Li/PAS and Li/graphite cells, impedance analyses were conducted. The interfacial

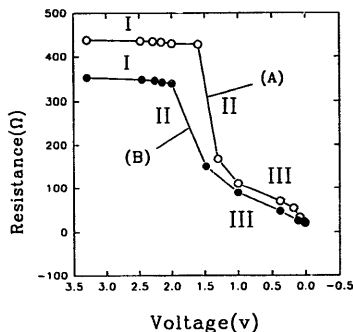


Fig. 6. Interfacial resistance ( $R_e$ ) between PAS or graphite electrode and electrolyte as a function of open-circuit voltage for (A) Li/PAS and (B) Li/graphite cells.

resistance ( $R_g$ ) between a PAS or graphite electrode and the electrolyte as a function of OCV for Li/PAS and Li/graphite cells is given in Fig. 6. It is obvious that the  $R_g$  change for both cells is similar; it proceeds in three stages with discharge. At first,  $R_g$  decreases slightly, then drops quickly and, finally, exhibits a steady decrease. These three steps correspond to the three reactions as mentioned above in Fig. 4. It should be pointed out that at the second step (i.e., in the formation of an electronic insulating layer on a PAS or a graphite electrode due to the decomposition of electrolyte) the interfacial resistance is reduced markedly. The interfacial contact between a PAS or a graphite electrode and the electrolyte is improved by the formation of an interfacial layer. This layer is an electronic insulator but allows ionic conduction. When the film is sufficient thick to prevent electron tunneling from PAS or graphite, the electrolyte decomposition is stopped. The decrease of  $R_g$  in the second step is the major reason for the reduced impedance of the Li/PAS or Li/graphite cells.

From above results, it can be concluded that, except for a much higher capacity, the electrochemical behaviour of PAS

is very similar to that of graphite. The higher reversible capacity of PAS is due to lithium-ion intercalation.

Typical charge/discharge profiles of an Li/PAS cell, under the condition of  $I_d = I_c = 0.5 \text{ mA cm}^{-2}$ , are shown in Fig. 7. The PAS anode exhibits an attractively high Faradaic efficiency when cycled between 0.0 and 2.0 V (after 12 cycles).

Two laboratory cells were made to show the application of PAS as an anode material in lithium-ion batteries. An  $\text{LiCoO}_2$  cathode material was used. The cells displayed a capacity as high as  $130 \text{ mAh g}^{-1}$ , as shown in Fig. 8 [11].

PAN-EC-BL-LiClO<sub>4</sub> was used as the electrolyte in one cell. Its conductivity is shown in Fig. 9. The curvature of the plot suggests that the data can be fitted satisfactorily by the Vogel-Tamman-Fuocher (VTF) equation over a broad temperature range. The electrolyte possesses a high conductivity, even at a low temperature.

Typical charge and discharge curves of cell (A) PAS/1 M LiPF<sub>6</sub>-EC-DEC/LiCo<sub>2</sub> and cell (B) PAS/PAN-EC-BL-LiClO<sub>4</sub>/LiCo<sub>2</sub> cells at room temperature are given in Fig. 10. Both types of battery display excellent reversibility when operated in the voltage range 4.2 to 3.0 V at a charge

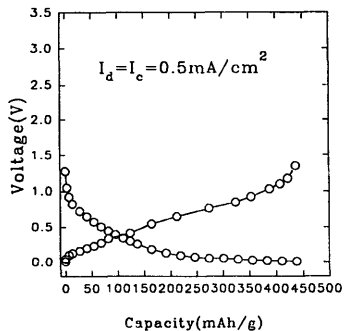


Fig. 7. Typical charge/discharge profiles of an Li/PAS cell under condition:  $I_d = I_c = 0.5 \text{ mA cm}^{-2}$ .

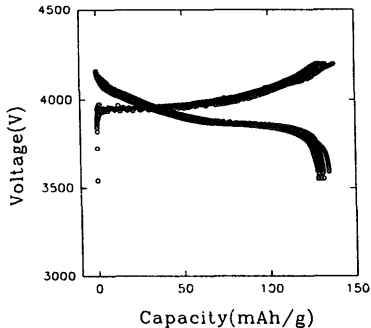


Fig. 8. Charge and discharge curves for Li/LiCo<sub>2</sub> cell under condition:  $I_d = I_c = 0.5 \text{ mA cm}^{-2}$ .

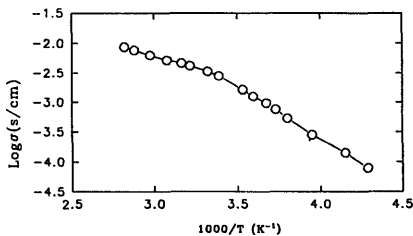


Fig. 9. Conductivity vs. temperature for 20PAN-35EC-40BL-SLiClO<sub>4</sub> (in weight ratio) electrolyte.

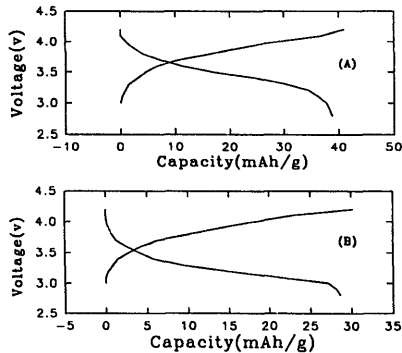


Fig. 10. Typical charge and discharge curves of cells: (A) PAS/1 M LiPF<sub>6</sub>-EC-DEC (1:1 in volume ratio)/LiCo<sub>2</sub> and (B) PAS/20PAN-35EC-40BL-SLiClO<sub>4</sub> (in weight ratio)/LiCo<sub>2</sub> under the condition:  $I_d = I_c = 0.4 \text{ mA cm}^{-2}$ .

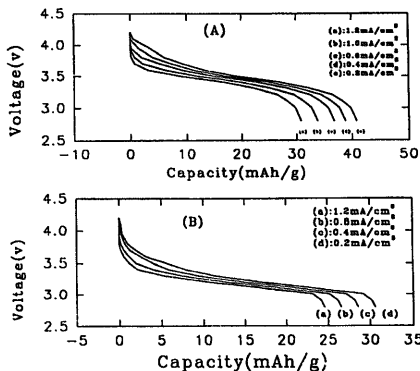


Fig. 11. Discharge profiles of: (A) PAS/1 M  $\text{LiPF}_6$ -EC-DEC (1:1 in volume ratio)/ $\text{LiCoO}_2$ ; and (B) PAS/20PAN-35EC-40BL-5 $\text{LiClO}_4$  (in weight ratio)/ $\text{LiCoO}_2$  cells at different current densities.

and discharge current density of  $0.4 \text{ mA cm}^{-2}$ . In this case, the batteries demonstrated a specific capacity of  $37 \text{ mAh g}^{-1}$  for cell (A) and  $28 \text{ mAh g}^{-1}$  for cell (B). The discharge profiles of cells (A) and (B) at different current densities are given in Fig. 11. It can be seen that even at a current density as high as  $1.2 \text{ mA cm}^{-2}$ , the test cells still have rather high capacities.

The discharge capacities of cells (A) and (B) as a function of cycle number are given in Fig. 12. The capacity of the test cells declines at an extremely low rate.

#### 4. Conclusions

It is concluded from these preliminary results that a battery with PAS anode material is a promising candidate. There is

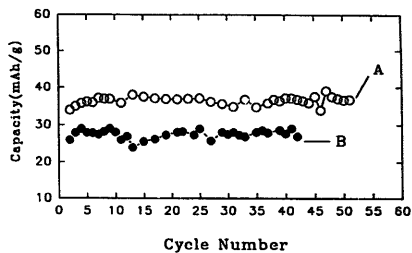


Fig. 12. Discharge capacity of (A) PAS/1 M  $\text{LiPF}_6$ -EC-DEC/ $\text{LiCoO}_2$  and (B) PAS/PAN-EC-BL- $\text{LiClO}_4$ / $\text{LiCoO}_2$  cells as function of cycle number.

considerable scope to improve on the present performance. Further studies are in progress in our laboratory.

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