PERFORMANCE OF POLYACRYLONITRILE-BASED CATHODES IN LITHIUM–IODINE SOLID STATE BATTERIES

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Summary

Vacuum-cyclised polyacrylonitrile (VC-PAN) has been prepared in the form of films and powders. The reactivity of these materials compared with halogens is high and when loaded with iodine, their electrical conductivity may reach a value of 10^{-2} ohm^{-1} cm^{-1}.

Experimental lithium solid state cells with cathodes based on VC-PAN/I_2 material have been assembled in the laboratory and standard CR 2016 button cells have also been manufactured. the cells have been discharged at various loads. At equivalent iodine loadings the film-based cathodes are characterized by better discharge properties (achieved capacities at higher current drain) than batteries using powder-based cathodes. The powder-type of cathodes, however, offer the advantage of superior nominal capacity due to their higher iodine loading

A strong dependence of the discharge properties with temperature was also observed and is reported.

Introduction

The thermal degradation of polyacrylonitrile (PAN) has generated a great deal of interest due to the use of PAN as a precursor to manufacture carbon fibers This process includes a low temperature treatment to cyclise adjacent nitrile groups and to form a ladder polymer [1].

Recent studies on the thermal treatment of PAN fibers under vacuum have confirmed the ladder structure of the resulting polymer, where the number of cyclised rings per fused unit is substantially *increased* [2, 3]. Consequently, vacuum cyclised PAN is a highly conjugated polymer and exhibits a structure of either polypyridinopyridine (1) or, most probably under these conditions, of polyhydronaphthalene (2) (Fig. 1).

Preliminary results of the conductivity of iodine-loaded PAN by other authors [1 - 3] suggest that VC-PAN–I_2 may be an attractive candidate for further studies as an active battery component, most likely in a lithium–iodine cell. This has already been demonstrated in our laboratory and was reported elsewhere [8 - 10].

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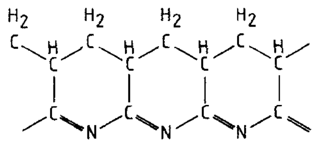
(1) 

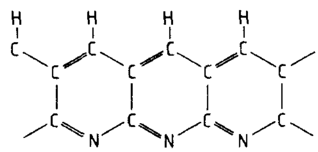
(2) 

Fig 1 Possible structures for the vacuum-cyclised polyacrylonitrile (VC-PAN) (1), polypyridinopyridine, (2), polyhydronaphthalene

Experimental

Polyacrylonitrile (PAN) films have been prepared by doctor-blade casting the polymer from DMF solution initially containing about 9% by weight of solid material. PAN is most conveniently taken as fibrous material (Courtaulds) but good results may also be obtained starting from Du Pont powders. Casting takes place on glass plates in a multistep process, with vacuum drying at 60 °C after each casting step. The nickel screen which is incorporated in the film is introduced after reaching approximately half the desired thickness (Exmet Ni of 50 μm)

For the cyclisation step the film is cut into discs, placed between Teflon* coated glass plates, and subjected to a programmed vacuum (0.01 - 0.005 Torr) heat treatment which includes a maximum temperature of 350 °C for 5 h

After storage in a dry box (<5 ppm water) for at least 24 h the sample is exposed to dry iodine vapour at temperatures between 80 and 120 °C in a glass vessel from which air and moisture have previously been evacuated The samples take up iodine to about five times the initial weight of polymer, usually in about two hours. For example, a nickel screen supported, 16.4 mm dia., 0.90 mm thick specimen with an initial weight of 100 mg of PAN contains, typically, 0.5 g of iodine

The vacuum cyclised films can also be crushed into powders (VC-PAN powders) which will be exposed to iodine vapour The natural iodine loading of the VC-PAN through the gas phase reaches a value slightly superior to two atoms of iodine per cyclised PAN unit. VC-PAN powders loaded with iodine can also be mixed with pure iodine in order to produce high iodine ratio powders such as 1.18 (VC-PAN to iodine)

The VC-PAN/iodine loaded samples (films and powders) were tested as cathodes in lithium-based solid state cells Experimental cells including a VC-

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*Registered trade name of Du Pont for PTFE

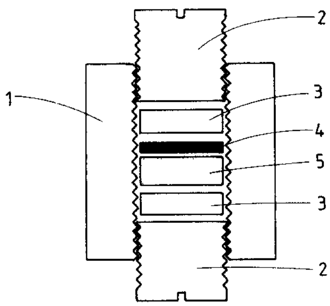

Fig 2 Schematic representation of the experimental assembly for the testing of Li/VC-PAN/I_2 batteries 1, Teflon–glass fiber reinforced body, 2, nickel screws, 3, nickel contacts, 4, lithium foils, 5, VC-PAN/I_2 cathode

PAN/I_2 cathode were assembled with a 0.5 - 1 0 mm thick lithium foil (see Fig 2). This stack was placed between two flat nickel contacts (3) which were pressed by nickel screws (2) in a threaded glass fiber reinforced Teflon body (1). The cell was tested under argon. Prototype button cells have also been assembled on a conventional Li/MnO_2 assembly line using standard CR 2016 or CR 2020 housings*.

Results and discussion

Film-based experimental cells

The film-based batteries have a cathode film of 0.3 mm thickness and 3.6 cm dia. after loading with iodine. The results obtained at discharge loads between 6 and 50 kΩ are represented in Fig. 3. Typically, at a 1.0 V cut-off up to 5 mA h cm^{-2} have been delivered.

Film-based button cells

When VC-PAN films thicker than 0.5 mm were produced, it became necessary to include a nickel grid or foam in the film during the casting process. This nickel current collector plays a double role:

(a) it gives additional mechanical support to the cathode, mainly during the loading process with iodine, and reduces the dimensional changes during the halogen uptake.

(b) it contributes to a better overall electrical conductivity and a more uniform current distribution through the thickness of the cathode

The thickness of the VC-PAN films was adjusted in order to fit within a CR 2016 standard housing. The average cathode characteristics are represented in Table 1

*The authors are grateful to Dr I Exnar of RENATA AG for his help in assembling Li/VC-PAN/I_2 CR 2016 and 2020 button cells

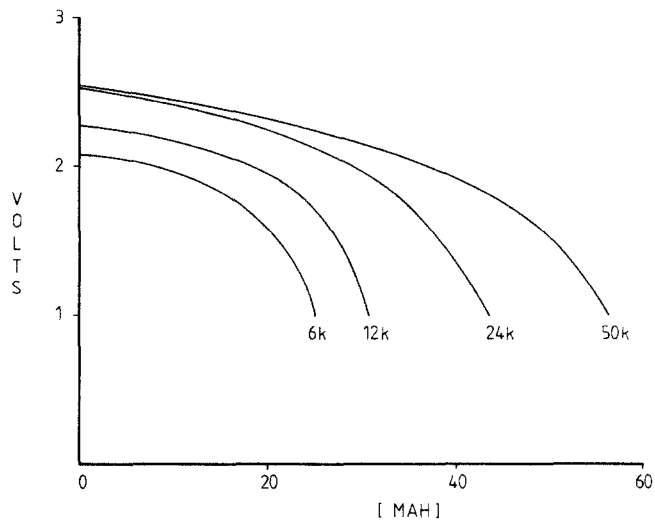

Fig 3 Achieved capacities at 22 °C of $Li/VC\text{-}PAN/I_2$ experimental cells Conditions unsupported cathode 10 cm^2 active area, constant load discharge, and cathode thickness 0 3 mm

TABLE 1

VC-PAN/I_2 cathode characteristics

	Supported film (for CR 2016 model)	Powder-type (for CR 2020 model)
Diameter (mm)	16 5	17
Thickness (mm)	0 9	0 93 - 1 00
Total weight (g)	0 600	0 780 - 0 820
Iodine/VC-PAN ratio	4 5 1	18 1
Iodine + VC-PAN weight (g)	0 480 - 0 520	0 780 - 0 820
Current collector weight (g)	0 080	—
Theoretical capacity (mA h) (based on iodine content)	104	160

The discharge curves obtained at various loads with this type of battery are shown in Fig. 4

Powder-based button cells

In an other set of experiments, the standard VC-PAN film was crushed to fine powder and loaded with iodine to various ratios. CR 2020 button cells were assembled with pelletized VC-PAN/I_2 powders; the discharge results obtained at 60 °C are presented in Fig 5(a) and (b). The characteristics of these cathodes are also presented in Table 1

From the analysis of these figures, it can be concluded that the achieved capacities are directly related to the initial iodine loading. A summary

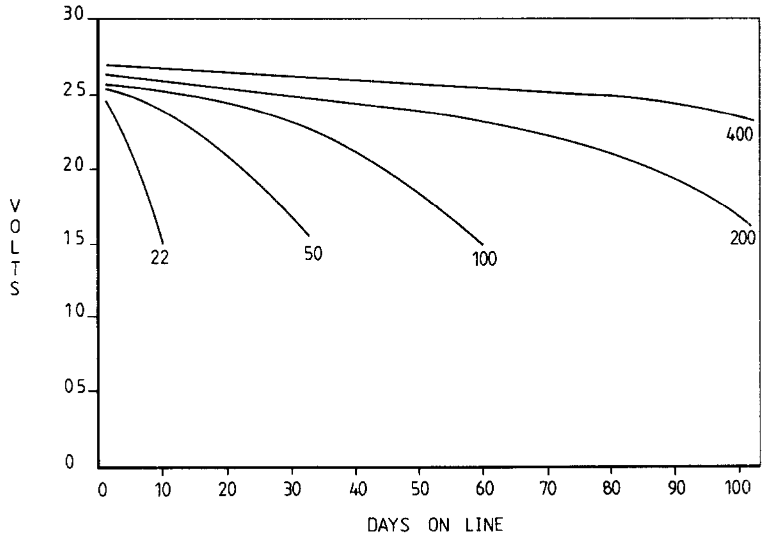

Fig 4 Discharge curves obtained at various loads with supported films cathode assembled in $Li/VC\text{-}PAN/I_2$ CR 2016 button cells

TABLE 2

Achieved capacities at various iodine loadings and discharge conditions expressed as a % of theoretical capacity (temp 60 °C)

Load in kΩ	I_2/PAN weight ratio			
	4 5	9 0	13 5	18 0
22	43	57	68	75
50	51	72	80	83
100	72	65	80	82
200	85	87	89	90

of the performance obtained at various iodine loadings and under different discharge conditions is presented in Table 2.

By comparison with the film-type batteries, the powder-type have a lower discharge capacity at lower discharge loads. It is the higher conductivity of the film-based cathodes which confers to this type of material the advantage of a higher current drain. It is known that a PAN cathode loaded with "4.5-times" iodine has a higher conductivity than the alternative cathode material loaded with a ratio of PAN/iodine of 1:18 [4].

Earlier published data [5, 6] show that the performance of the Li/I_2 system is strongly influenced by the nature and the morphology of the LiI electrolyte layer which is formed during the discharge of the battery.

Although not demonstrated, it is possible to consider the polymer

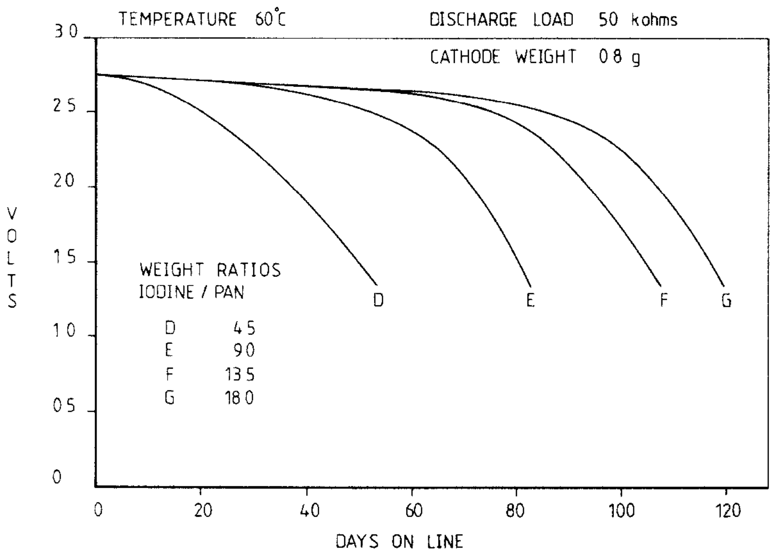

Fig 5(a) Discharge curves obtained at 50 kohm loads for different iodine loadings of the the cathode material

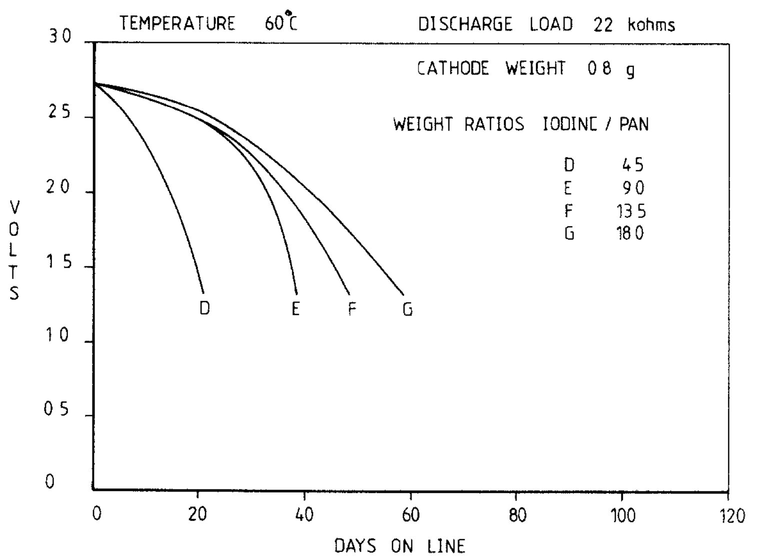

Fig 5(b) Discharge curves obtained at 22 kohm loads for different iodine loadings of cathode material

structure as playing a role in the conductivity of the LiI electrolyte layer (as suggested recently by Jolson *et al* in the case of P2VP/I_2 batteries [7]).

The influence temperature has on the discharge properties is shown in Fig. 6. This is in agreement with the variation of conductivity with temperature of the lithium iodide solid electrolyte which is formed during discharge.

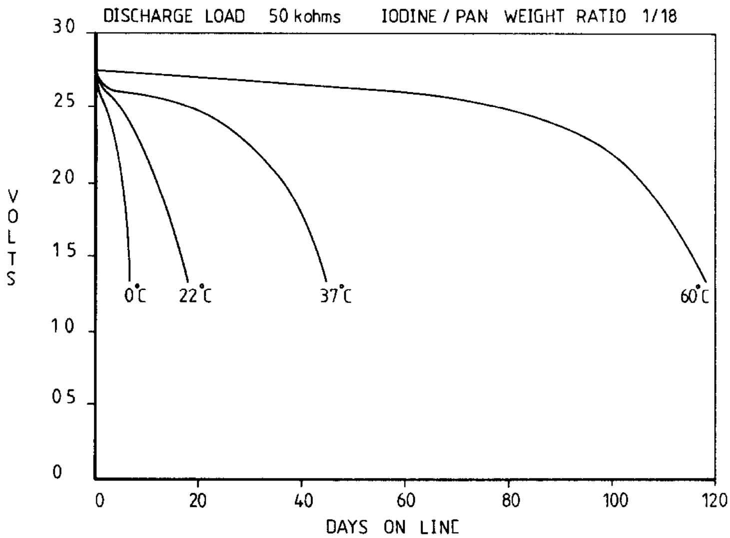

Fig 6 Temperature dependence on the discharge properties of the $Li/VC\text{-}PAN/I_2$ battery

Conclusions

In the $Li/VC\text{-}PAN/I_2$ system, cathode materials with a loading of two iodine atoms per cyclised PAN unit have high current drain characteristics. When higher iodine loading cathode materials are produced, their characteristics are much closer to the conventional $P2VP/I_2$ system. The $VC\text{-}PAN/I_2$ cathode appears to be able to perform closest to theoretical capacity when the system is discharged at a temperature of 60 °C in a discharge load range of 22 kΩ to 200 kΩ.

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