LITHIUM–IODINE BATTERIES BASED ON METAL DIBENZO(b,ı)-1,4,8,11)TETRAAZA(14)ANNULENE–IODINE CHARGE TRANSFER COMPLEXES

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Summary

Metal dıbenzo(b,ı)(1,4,8,11)tetraaza(14)annulene–ıodıne charge transfer complexes show high electrical conductıvıty even ın the presence of a large excess of molecular ıodıne Investıgatıons of the behavıour of these materıals as cathodes ın lıthıum–ıodıne batteries ıs reported The ease of preparatıon and handlıng as well as the dıscharge characterıstıcs make ıt a potentıal alternative to the P2VP poly(2-vınylpyrıdıne)–ıodıne system.

Introduction

Since its introductıon ın the early seventıes by Catalyst Research Corporatıon [1], the lıthıum–ıodıne cell based on P2VP has become the standard power source for the heart pacemaker ındustry [2] The development of these cells as a pacemaker power supply has been successful because the solıd electrolyte LıI has a unıque combınatıon of ıonıc conductıvıty, electronıc resıstance, thermodynamıc stabılıty, and the capabılıty of being formed *ın sıtu* by the dırect combınatıon of the electrode materıals, while also formıng as the product of the dıscharge reactıon In these cells P2VP plays a dual role It ıs an electronıc donor system that forms conductıng complexes wıth ıodıne and thus elımınates the need to add conductıng fıllers such as carbon black or metal powders when employed as cathode materıal P2VP also serves as a matrıx to hold addıtıonal quantıtıes of molecular ıodıne as a reservoır for the cell reaction.

The system has been studıed and ımproved by several organızatıons and has been the subject of many patent applıcatıons [3] Because only a few companıes are ın a strong patent posıtıon there has been world-wıde research actıvıty by other groups to fınd substıtutes for the P2VP system and thereby

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to enter the fast growing pacemaker market Although a great number of other polymeric and monomeric donor systems form charge transfer complexes which are, in principle, suitable for application in lithium–iodine cells, none is commercial. The reasons may be sought in the variety of conditions which must be fulfilled by a cathode material, e g , chemical inertness of the matrix towards iodine (full reversibility of iodine "doping"), high electrical conductivity at both very high and very low iodine contents, ease of handling and preparation, low hygroscopy, etc From our work in the field of organic conductors we are aware that many of these boundary conditions can be met by the highly conducting charge transfer system dibenzo(b,i)(1,4,8,11)tetraaza(14)annulene–iodine [4, 5]

We report here on the results obtained using lithium–iodine cells incorporating these charge transfer complexes as cathode materials.

Experimental

Preparation of annulenes
Metal dibenzo(b,i)(1,4,8,11)tetraaza(14)annulenes (abbreviated M(dbtaa)) were prepared by published methods [6] from metal acetates, 1,2-phenylenediamines, and 1,1,3,3-tetraalkoxypropanes or dimethylamino-acroleins in high yields. The crude products were washed with warm water, ethanol, and ether, and vacuum dried at 100 ℃

Preparation of charge transfer (CT) complexes with iodine
M(dbtaa)'s spontaneously form CT-complexes upon contact with iodine Practical samples can be prepared by one of several methods
— stirring powdered M(dbtaa) in a solution of iodine in an inert solvent,
— exposing M(dbtaa) to iodine vapour at reduced pressure (e g , 20 mmHg),
— mechanically mixing solid iodine and M(dbtaa) together in a ball mill or lab mixer (preferably at reduced temperatures),
— mixing solid M(dbtaa) into molten iodine at 120 - 150 ℃
The last two methods are the most frequently used, especially for battery applications.

Iodine vapour pressure
The iodine vapour pressures of Ni(dbtaa)–iodine CT-complexes were determined as a function of iodine concentration by the flow method described by Marti et al [7]

In a typical measurement, between 250 and 600 mg of CT-complex were mixed with 70 g of glass beads and placed into the sample compartment of the apparatus. Purified nitrogen was used as carrier gas at a rate of between 2 and 10 l h^{-1} at 25 ℃. Iodine removed from the sample was absorbed in n-hexane and quantitatively determined photometrically at 522 nm.

Conductivity measurements

Electrical conductivities of CT-complexes were determined by the 2-probe technique using glass capillaries of 1 and 2 mm i d with stainless steel stamps

Cathode preparation

Ni(dbtaa) was vacuum dried and mixed with iodine (Merck p a) in molar ratios Ni(dbtaa) I_2 = 1 2 5 to 1 20 Some cathode mixtures were obtained by blending powdered annulene into molten iodine Cathode-shapes were made by pressing the mixture, under a pressure of 2600 kg cm^{-2}, between two polyethylene foils into a pellet of 1.7 cm in diameter and approximately 1 mm thickness All cathode preparations were carried out in an argon-filled drybox

Cell preparation

The cell used in these studies was a crimp-sealed coin type (20 mm dia , 2 mm high) as shown in Fig 1 The anode was made from Lithco high purity lithium foil and was directly pressed into a stainless steel can The pressed cathode was supported by a non-stainless steel current collector The theoretical capacity of the anode was 320 mA h and that of the I_2-cathode 135 mA h The electrode area was 2.26 cm^2 Sealing was accomplished using a polypropylene insulating ring under dry argon
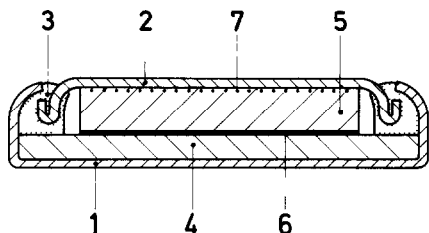

Fig 1 Cross-sectional view of an experimental Li/I_2 cell 1, Anode can, 2, cathode can, 3, insulating ring, 4, lithium anode, 5, cathode, 6, solid electrolyte LiI, 7, current collector

Battery performance

Cells have been discharged under constant resistive load The a c impedance measurements were made using 200 mV r m s sine waves at a frequency of 1000 Hz

Results and discussion

Table 1 shows typical conductivities of M(dbtaa)−iodine CT-complexes, prepared by mechanical mixing of the powdered compounds or by mixing powdered M(dbtaa) in molten iodine, measured at room temperature immediately after mixing Conductivities of the order of 10^{-2} - 10^{-3} S cm^{-1}

TABLE 1

Pressed pellet conductivities of M(dbtaa)/I_2 mixtures at 25 °C
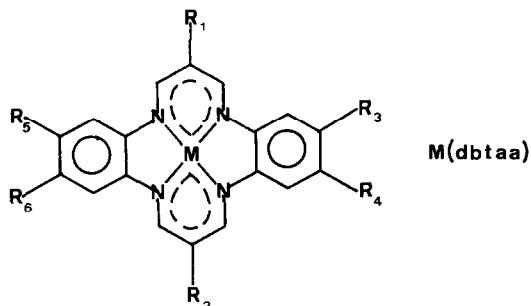
M(dbtaa)

M	R_1, R_2	R_3	R_4	R_5	R_6	Mole ratio M(dbtaa) I_2	Pressed pellet conductivity (S cm^{-1})
Ni	H	H	H	H	H	1 0 1	1×10^{-5}
Ni	H	H	H	H	H	1 3 9	$1\,5 \times 10^{-2}$
Ni	H	H	H	H	H	1 10	1×10^{-2}
Ni	H	H	H	H	H	1 53 2	$2\,5 \times 10^{-3}$
Ni	H	H	H	H	H	1 200	2×10^{-5}
Cu	H	H	H	H	H	1 21 8	$3\,3 \times 10^{-3}$
Ni	CH_3	H	H	H	H	1 10	1×10^{-3}
Ni	CH_3	H	H	H	H	1 65 6	9×10^{-4}
Ni	CH_3	CH_3	H	CH_3	H	1 75 5	$9\,6 \times 10^{-4}$
Ni	CH_3	CH_3	CH_3	CH_3	CH_3	1 113 3	$1\,6 \times 10^{-3}$
Ni	p-Toluyl	H	H	H	H	1 88 3	7×10^{-4}
Ni	H	—CH=CH—CH=CH—		—CH=CH—CH=CH—		1 44 8	4×10^{-4}
Fe	CH_3	H	H	H	H	1 20 4	$4\,5 \times 10^{-2}$

are achieved for iodine contents ranging from a few weight % to approximately 98% The probable reason for this surprising behaviour is that iodine is incorporated into the M(dbtaa) lattice between the M(dbtaa) stacks [4] thus leaving the conducting pathway along the partially oxidized extended M(dbtaa) stacks intact

In mixtures with very high iodine contents we are dealing essentially with an iodine matrix containing M(dbtaa) stacks as a filler showing very large geometrical anisotropy resulting in a low percolation threshold. This is comparable with the filling of plastics with conducting fibers or dendrite like CT-complexes [8] Here, high conductivities were observed at filler levels of only around 1% This behaviour is almost ideal for LiI battery applications in that the resistance of the cathode material will stay practically constant during the life span of the battery and negligible compared with the resistance of the LiI solid electrolyte

The doping process for M(dbtaa)s with iodine is very fast High iodine contents and high conductivities are achieved in a few hours when M(dbtaa)s

are exposed to iodine vapour Equally, dry mixing of M(dbtaa)s and iodine results almost instantaneously in highly conductive compounds The conductivity of such dry mixtures improves only slightly over the next 3 days when the maximum is reached This means that cathode materials prepared by dry mechanical mixing of M(dbtaa)s and iodine can immediately be used for the preparation of cells which can be fully used at once. In comparison, dry mixtures of P2VP and iodine take a longer time to develop the maximum conductivity [9] and cells so prepared can only be discharged at a reduced rate unless the batteries are annealed at elevated temperatures. Equally, doping of nickelphthalocyanine with iodine, a system also considered for LiI batteries [10], is a very slow process both in the vapour phase* and in iodine solution [10]

    M(dbtaa)s are capable of binding large amounts of iodine in their crystal lattices They behave like iodine sponges, absorbing many times their own weight of iodine One method of determining the maximum equilibrium uptake makes use of partial vapour pressure measurements Figure 2 shows the partial vapour pressure of Ni(dbtaa)–iodine complexes at 25 °C The equilibrium iodine content (where one measures the vapour pressure of the free iodine) at ambient pressure and 25 °C is around 86 to 88 mole% for several samples corresponding to a molar ratio of Ni(dbtaa) I_2 of roughly 1 7 to 1·6 Below this threshold the vapour pressure decreases to a value of
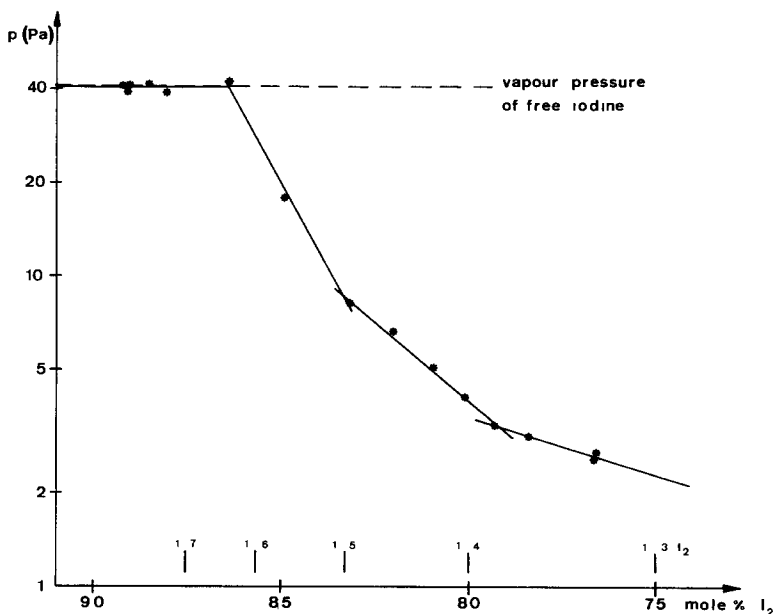

Fig 2 Iodine partial vapour pressure of Ni(dbtaa)–I_2 mixtures at 25 °C, semilogarithmic plot, vapour pressure in pascals

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    *Iodine content of nickelphthalocyanine after 4 1/2 days in iodine atmosphere at 20 mmHg, RT 6%, of Ni(dbtaa) under the same conditions 81%

4×10^{-1} Pa at 60 mole% This is one hundred times lower than that of free iodine but is still significant, suggesting easy availability of iodine for the cell reaction In this semi-logarithmic plot one can identify linear parts of the vapour pressure curve roughly coinciding with molar ratios of 1 6, 1 5, 1 4 and 1 3

The preparation of lithium–iodine cells with these cathode materials is simple and straightforward (Fig 1) Pellets of cathode material and lithium, each contained in a stainless steel cup, are pressed together and crimp sealed using a polypropylene gasket. Surprisingly, these cells proved to be iodine tight for up to 2 years at room temperature Long term hermetic sealing, however, especially at higher operating temperatures, can only be achieved with welded cases and glass–metal contacts

Although cells were prepared with various dbtaas, the unsubstituted nickel complex, Ni(dbtaa), proved to be the most suitable, both commercially and with regard to performance Molar mixing ratios of Ni(dbtaa) with iodine were varied over the range 1 2 5 to 1 20 Ratios of $1 \cdot 2\,5$ are too low for practical purposes, giving unsatisfactory battery capacity. On the other hand, dry mixing and tablet pressing of Ni(dbtaa) and iodine in molar ratios greater than approximately 1 15 (~92 wt % iodine) proved to be difficult since the solid state properties of the mixture are completely dominated by the ductile iodine matrix The ideal range giving high capacity and easy processability lies between 1 10 and 1 15. Most experiments were performed with batteries containing cathodes of Ni(dbtaa)· 10 I_2 (88 wt % I_2, 91 mol%) The open circuit voltage of these cells at room temperature was 2 80 V

The discharge behaviour for 2020 button cells under various conditions is shown in Figs 3 and 4 At room temperature the cells perform best at discharge rates of a few μA to roughly 20 μA Higher discharge rates of 50 μA or more are possible at elevated temperatures, while discharging at 0 °C allows a drain of only up to 5 μA It is a characteristic of these systems that the internal resistance of the cells (LiI solid electrolyte) grows continuously
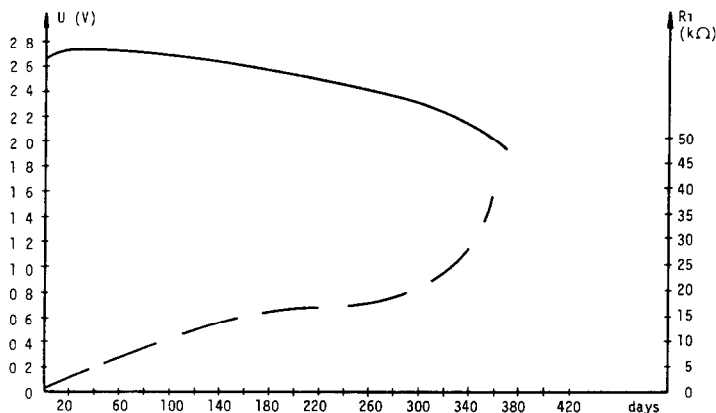

Fig 3 Discharge curve and cell impedance of Li/Ni(dbtaa) 10 I_2 at RT 243 kΩ constant load
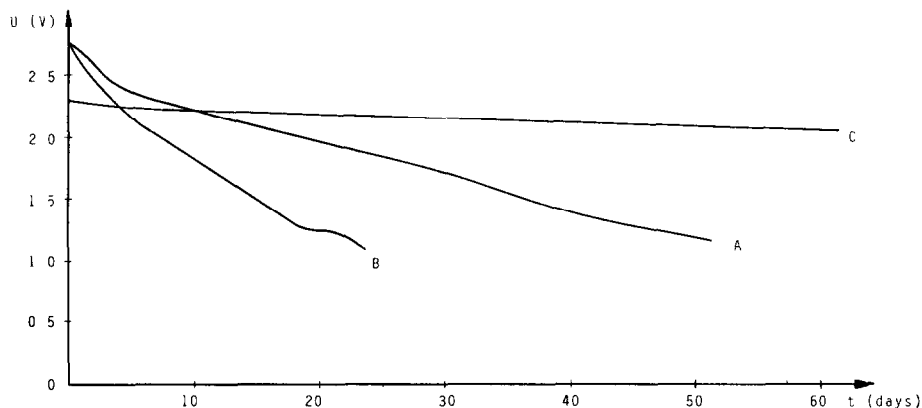
Fig 4 Discharge behaviour of the 2020 experimental cell using Ni(dbtaa) 10 I₂ cathode at 80 °C A, 47 kΩ, B, 22 kΩ, C, 390 kΩ at 0 °C

during the discharge reaction (Fig 3) and is a limiting factor for the discharge rate Typical applications for these batteries are low drain devices such as memory back up and heart pacemarkers.

Conclusion

Although the Li/Ni(dbtaa)—iodine system has not been fully developed, the present data make it a potential alternative to today's Li/P2VP—iodine cells. Further development is, however, needed and questions such as the influence of particle size distribution, water content, and low level impurities in Ni(dbtaa) on discharge and self-discharge will have to be answered Also, the reason for an unsatisfactory discharge behaviour under load in some cells (less capacity, faster voltage decline than average) has to be established

Acknowledgements

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