An all-polymeric solid state battery

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Doped polyacetylene is one of the very important recently discovered materials in polymer science. It has been found that polyacetylene, $(CH)_x$, may be chemically doped with either p- or n-type dopants to give a series of semiconductors, and even transformed into a polymeric metal[1–6]. Several devices have been made using its semiconducting properties and its ready acceptance of various dopant species[7–10]. The ability of a $(CH)_x$ film to incorporate large quantities of dopants is of interest. For example a $(CH)_x$ film can be doped with 10 mol% Iodine[6], 7 mol% AsF_5[3] or over 12 mol% alkali metals[7]. The doped film can achieve high conductivity ($\sigma > 1$ S cm^{-1}) with about 1 to 2 mol% of dopant concentration[1]. All of these dopings can be done at room temperature[1–6]. The doping behaviour of the $(CH)_x$ film is remarkably different from that of high mobility semiconductors, for which only trace amounts of impurities produce relatively high conductivities and for which doping requires a high temperature environment[11]. The high atomic ratio of dopant to the host polymer makes doped $(CH)_x$ a potential electrode material for battery applications[12], and a rechargeable storage battery has already been made using $(CH)_x$ films with $LiClO_4$ solution as the electrolyte[8,9].

In this communication we report that the doping of $(CH)_x$ films can also be brought about in a wholly solid state reaction at temperatures higher than room temperature. Therefore, an all-polymeric solid state battery can be constructed using $(CH)_x$ films and a polymeric solid electrolyte. Preliminary experimental results obtained from cells made of $(CH)_x$ films as the electrodes and polyethylene-oxide-sodium-iodine complex as the electrolyte gave a power density of 10–20 watts kg^{-1}, in this all-polymeric battery.

Polyacetylene films of typical thickness 0.1–0.2 mm and density 0.4 g/cc, were prepared by the method as reported by Shirakawa *et al.*[13,14]. These films had been stored for a period of time in a sealed glass tube at room temperature. This as-grown *cis*-$(CH)_x$ film contained typically 80% *cis*- and 20% *trans*-isomer. The wholly *trans*-$(CH)_x$ film was obtained by the cited methods of isomerization[13]. both *cis*- and *trans*- films had been used in the experiments reported here. Handling of the film was done mostly under argon atmosphere, but the film was exposed to air in certain cases. In general, long term air exposure of $(CH)_x$ causes decay of its conducting properties. In these preliminary experiments some oxidation effects undoubtedly occurred, but did not mask the essential electrochemical behaviour.

The polyethylene-oxide, PEO, of molecular weight 5×10^6, was available commercially. The PEO-alkali metal complexes were prepared as described by Armand *et al.*[15]. These PEO complexes have been shown to be solid electrolytes[15,16]. The ionic conductivity of these polymers is high enough to be used at relatively low temperature. The electrical conductivity of one such PEO–NaI complex with Na/O = 0.2, for example, was 1×10^{-4} S cm^{-1} at 85°C. The complex has a reasonable chemical stability. The PEO complex was processed into the form of a free standing film of thickness 0.1–0.2 mm for the battery construction. We shall return to this topic after a description of solid state doping of a $(CH)_x$ film.

Doping of $(CH)_x$ films was first demonstrated using dopants in the gas phase[1–3]. It has been found that $(CH)_x$ films could also be doped when they were immersed in a solution which contained the dopant as solvent[2–4]. Recently, electrochemical doping processes using electrolyte solution were reported[8,9]. A $(CH)_x$ film was used as an electrode in an electrolytic cell, and the doping was achieved and controlled by the electrical current or potential[8]. The electrochemical reactions are not restricted to liquid electrolytes, but could in principle be done using a solid electrolyte. For solid state electrochemical doping, an n-type dopant ion D^+ could react with the $(CH)_x$ film at the cathode according to

$$(CH)_x + xy\,D^+ + xy\,e^- \rightleftarrows (CHD_y)_x \qquad (1)$$

Reasonably high ionic conductivity in the electrolyte is an essential factor for the electrochemical doping to be practical. Most solid electrolytes have very small ionic conductivity at room temperature, and the electrolytic solutions are generally much better ionic conducting media. Only a limited number of fast ionic conductors are available for solid state electrochemical reaction with $(CH)_x$. Polyethylene-oxide complexes have been selected for this demonstration, because of their potential for light-weight solid electrolytes for future applications. The solid state doping of $(CH)_x$ was demonstrated using the cell

$$(CH)_x|\text{PEO-NaI}|\text{Na} \qquad (2)$$

under dynamic vacuum at 85°C. The *cis*-$(CH)_x$ film was equipped with two electrodes to measure the resistance of the film and determine the doping effect. By applying a fixed electrical potential of a few volts across the terminals of the cell, the Na ions were attracted to the $(CH)_x$ film, and reduced the film. The resistance of the $(CH)_x$ film decreased as the doping progressed. The measurement of the cell resistance as well as the resistance of the $(CH)_x$ film confirmed a decrease of five orders of magnitude in the resistivity. The doped $(CH)_x$ film had no visible change of colour and remained flexible. The conductivity of sodium doped $(CH)_x$ films has been shown by a study of the chemical line shift of n.m.r. signals not to be caused by metallic sodium[17]. Full experimental details of the solid state doping will be published elsewhere.

To construct all-polymeric solid state batteries we used cells given either by equation (2) or others given by equation (3) and referred to here as cell (3).

$$(CH)_x|\text{PEO-NaI}|(CH)_x \qquad (3)$$

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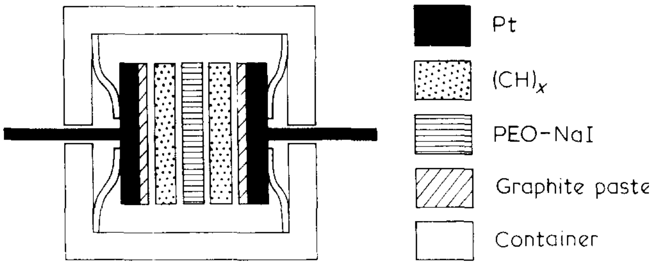

Figure 1 Schematic structure of an all-polymeric solid state battery

The configuration is sketched in *Figure 1*. The PEO–NaI film was sandwiched between two $(CH)_x$ films of the same size. The manipulations were performed in a glove bag in an argon atmosphere. Electrical contacts to the $(CH)_x$ films were made using graphite paste and platinum plates. External electrical leads were attached using mechanical pressure. The assembly was housed in a sealed or evacuated container for further tests. A typical battery had an effective area between 0.15 and 0.6 cm^2. The total weight of the active battery materials varied from 5 to 30 mg. The battery of equation (2) was made with a platinum or aluminium reservoir for sodium metal.

Several polymeric batteries were tested at 85°C. The cell (2) could be thought of as a solid state battery assembled in a fully charged state for which a partial discharge (doping) was required to build up the conductivity of the cathode to make the battery useful. When the cell was discharged in this way for the first time, the solid state electrochemical doping converted the pure $(CH)_x$ film at the cathode to a Na-doped $(CH)_x$ film. Cell (2) became

$$(\mathrm{CHNa}_y)_x|\mathrm{PEO{-}NaI}|\mathrm{Na} \qquad (4)$$

The cell (3), however, required electrochemical doping to convert into a cell

$$(\mathrm{CHNa}_y)_x|\mathrm{PEO{-}NaI}|(\mathrm{CHI}_z)_x \qquad (5)$$

where y depended on the total charge passed, and z, the iodine doping of the anode. It was clear that $(CHNa_y)_x$ and $(CHI_z)_y$ could also be used directly for constructing the battery. This might make it possible to increase the capacity of the battery[8,9].

The open circuit voltage, V_{oc}, of the battery was measured using an electrometer and a chart recorder. The short circuit current, I_{sc}, was measured using a multimeter directly. A typical V_{oc} of an all-polymeric solid state battery of cell (4) or cell (5) ranged from 2.8 to 3.5 volts. The I_{sc} of these batteries varied from 1 to 12 mA cm^{-2}. *Figure 2* illustrates several short term charge–discharge curves of a $(CH)_x|PEO–NaI|(CH)_x$ battery. These measurements were made after a number of initial charge–discharge cycles of the battery. During a charging cycle, a constant charging current of 0.1 mA was applied for one minute. The charged battery was discharged through a resistance load in series with a multimeter. The cycle was repeated after one minute of discharge. From these initial charge–discharge curves, we estimated the power density of this battery to be 10–20 watt kg^{-1}. For this polymeric battery there was no significant decay in its characteristics after over 20 charge–discharge cycles. There was no visible change in the colour of the $(CH)_x$ or its flexibility. The colour of the PEO–NaI complex became yellow-brown, probably due to the iodine.

The observed V_{oc} of the $(CH)_x|PEO–NaI|(CH)_x$ cell is comparable with those obtained in liquid-electrolyte batteries[8,9]. The I_{sc} of this experimental cell is about 3 times smaller than those obtained in the liquid cells. These solid state cells also have smaller power and energy density than those of solution cells. The maximum power density observed was 250 watt kg^{-1} in a Na|PEO–NaI|$(CH)_x$ cell. The cell was discharged through a 2×10^3 ohm resistance load. The discharge current was 3 mA cm^{-2} initially and decreased to about half in 15 min. The current decreased to 0.5 mA cm^{-2} after 1 h. The mass of sodium $(CH)_x$ and PEO–NaI complex was about 0.012 g. Thus, we obtained an energy density approximately 20 watt-hour kg^{-1} for this cell. The internal resistance of the experimental cells is relatively high. It is probably due to electrode/electrolyte interface effect and the conditions of solid state doping of $(CH)_x$ films[8,9,18,19].

In summary these preliminary experimental results demonstrated that an all-polymeric solid state battery can be made from a suitable polymeric semiconductor such as polyacetylene and polymeric solid electrolytes such as polyethylene-oxide complexes. The power density and the energy density produced in these batteries has potential for practical use.

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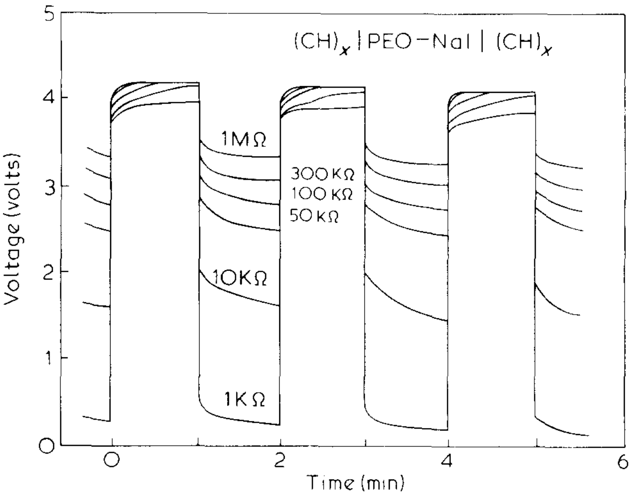

Figure 2 Constant current charge–discharge curves of $(CH)_x$|PEO–NaI|$(CH)_x$ battery. The charging current is 0.1 mA and the discharging loads are shown in the figure

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Complex formation between poly(vinyl alcohol) and borate ion

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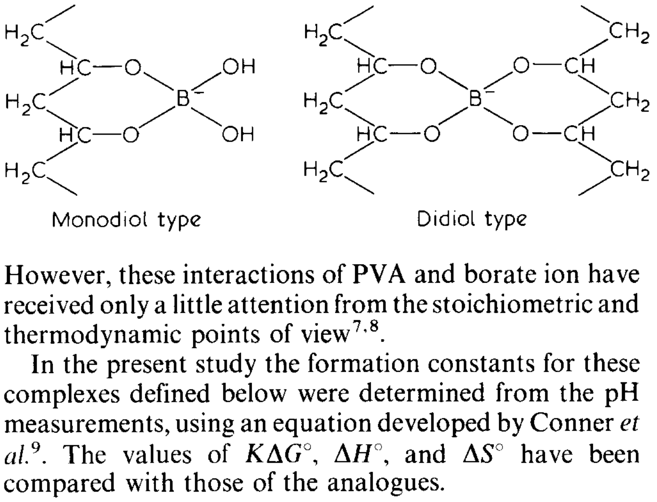
Introduction

Numerous studies have been carried out on the aqueous poly(vinyl alcohol) (PVA)–borate systems to interpret their thickening and gelling phenomena[1]. It is generally believed that these phenomena result from the complex formation of monodiol or didiol types between the OH groups of PVA and borate ion, similar to those in the simple low-molecular-weight polyol–borate systems[2–6].



Monodiol type

Didiol type

However, these interactions of PVA and borate ion have received only a little attention from the stoichiometric and thermodynamic points of view[7,8].

In the present study the formation constants for these complexes defined below were determined from the pH measurements, using an equation developed by Conner *et al.*[9]. The values of $K\Delta G^\circ$, ΔH°, and ΔS° have been compared with those of the analogues.

$$B^- + P = BP^-, \qquad K_1 = [BP^-]/[B^-][P] \qquad (1)$$

$$B^- + 2P = BP_2^-, \qquad K_2 = [BP_2^-]/[B^-][P]^2 \qquad (2)$$

where B^- is the borate ion, and P is PVA expressed in 2 monomer units. BP^- and BP_2^- are monodiol and didiol types of complexes, respectively. [ ] denotes the concentration expressed in mols per litre.

Experimental

The sample PVA (fully hydrolysed grade) was crudely fractionated into three fractions with n-propanol–water systems. The middle fraction, which was used as the sample in the present study, was treated with aqueous sodium hydroxide to complete saponification, and was purified by dialysis. Thus obtained, the material did not show any characteristic absorption band corresponding to a residual acetyl group in its i.r. spectrum. The degree of polymerization estimated from viscosity measurements was about 500. Anhydrous borax (sodium tetraborate) ($Na_2B_4O_7$) was used after heat-treatment (Suprapur, Merck). CO_2-free conductivity water was always used. All the reaction mixtures were prepared by a procedure previously described[9,10], and allowed to set in a nitrogen atmosphere for at least 1 day to attain the complexing equilibrium prior to pH measurements.

Measurements of pH were made with a TOA model HM-18E pH-meter, using a GST-155C combination electrode. All measurements were carried out in a nitrogen atmosphere to prevent CO_2-contamination, using a conventional water bath to give a temperature control of ±0.05° at 10°, 25°, and 35°C. The meter was standardized separately at each working temperature with standard buffers. A correction for the medium was not made since the PVA concentration was not high.

Results and Discussion

The results of pH measurements at three temperatures are presented in *Figure 1* as a function of PVA concentration expressed on the basis of mols of 2 monomer units per litre. A set of curves indicates the increasing acidity of boric acid with increasing PVA concentration, and this trend is greater at lower temperatures.

An equation developed by Conner *et al.* for the simple polyol–borate complexes may be useful in measuring the complexing ability between PVA and borate ion. The theory behind the derivation of the equation is that the complexation increases the acidity of boric acid and this increase is dependent on the complexant (PVA) concentration. Furthermore, it is assumed that the amount of unionized boric acid [HB] does not significantly change with PVA concentration and remains

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