Use of Polymer–Iodine Adducts as Positive Electrodes of Cells

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Summary Polymer [poly(*N*-vinylcarbazole), poly(vinyl alcohol), *etc.*]–iodine adducts can be used as the positive electrodes of cells.

Although the high electronegativity of iodine suggests that it could be used as a positive electrode in a cell, its usefulness is restricted by its high electric resistance and by the difficulties in moulding pure iodine. Recently several papers[1] reported that some polymers absorb iodine to give electrically conducting polymer–iodine adducts. This finding suggests that the disadvantages in using iodine for positive electrodes could be overcome by supporting iodine on polymers, since polymeric materials can, in general, be moulded easily. This paper deals with the application of polymer–iodine adducts for positive electrodes of cells.[2]

Initial electromotive forces and electric currents of cells composed of the polymer–iodine adducts as the positive electrodes and metals as negative electrodes are shown in the Table. A mixture of poly(*N*-vinylcarbazole) (15 mg) and iodine (7 mg) was ground in an agate mortar, and the resulting reddish-brown powder was moulded into a disk (ϕ 10 mm) by pressing it at 600 kg/cm^2. This disk and zinc foil were immersed in an aqueous solution of ZnI_2 (0·06 mol/l), the areas (one side) of the polymer–iodine disk and the zinc foil immersed in the aqueous solution being *ca.* 0·5 cm^2. A voltmeter and an ammeter showed that an electric current (1·2 V, 1·2 mA) flowed when the two electrodes were connected to each other. The voltage and electric current gradually decreased and the values became 0·6 V and 0·5 mA, respectively, after 1 h (total electricity after 1 h: *ca.* 3 C). Similar cells were obtained using other polymer–iodine adducts as listed in the Table. Aqueous solutions of almost all of the electrolytes tested were usable as the medium, but sometimes partial dissociation of iodine from the polymer-iodine adducts and dissolution of iodine into the aqueous solution (presumably as I_3^-) were observed when iodides such as ZnI_2 and MgI_2 were employed as the electrolyte and the polymer did not have a strong affinity toward iodine. Among the polymers tested, poly(2,5-thienylene) seemed to absorb iodine most strongly and in this case no apparent dissociation of iodine was observed even when iodides were employed as the electrolyte.

Table. Employment of polymer–iodine adducts as positive electrodes of cells.

Polymer support	Weight % of iodine	Negative electrode	Electrolyte[a] (mol/l)	Initial voltage /V	Initial electric current /mA
Poly(*N*-vinylcarbazole)	32	Zn	ZnI_2 (0·06)	1·2	1·2
Poly(vinyl alcohol)[b]	50	Zn	ZnI_2 (0·23)	1·3	2·0
Poly(vinyl alcohol)[b]	50	Zn	NaCl (0·08)	1·3	2·0
Poly(vinyl alcohol)[b]	50	Mg	MgI_2 (0·07)	1·2	1·8
Poly(vinyl pyrrolidone)[b]	18	Zn	ZnI_2 (0·03)	1·3	3·0
Poly(2,5-thienylene)	34	Zn	ZnI_2 (0·06)	1·4	1·5
Poly(2,5-thienylene)	34	Zn	NaCl (0·35)	1·3	1·3
Poly(2,5-thienylene)	34	Zn	KCl (0·32)	1·3	1·3

[a] Aqueous solutions of the electrolytes were used. [b] The shape of the positive electrode was gradually destroyed by dissolution of the polymer in the aqueous solution. In these cases it is necessary to use copolymers with divinylbenzene in order to avoid the dissolution of polymers.

The present system can be applied to secondary cells, too. *E.g.*, when an aqueous solution of MgI_2 (0·07 mol/l) was electrolysed at 3 V using poly(2,5-thienylene) [37 mg, moulded into a disk (ϕ 10 mm) at 600 kg/cm^2] as the anode and magnesium foil as the cathode, *ca.* 300 mC of electricity flowed in 5 min and iodine formed on the anode was absorbed on poly(2,5-thienylene). The secondary cell thus formed showed an e.m.f. of 1·5 V.

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[2] T. Yamamoto, Japanese Pat., applied No. 55–089492 (1st July, 1980).