

A study of some charge transfer complexes as electrodes in solid-state cells

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The electrical and electrochemical properties of charge transfer complexes of iodine with o-tolidine, phenothiazine and N-methylphenothiazine have been investigated with a view to determining their suitability as electrodes in cells based on solid electrolytes. Discharge and polarization studies have shown that iodine electrodes based on phenothiazine and N-methylphenothiazine offer excellent prospects as practical cathodes.

1. Introduction

Charge transfer complexes, formed by the interaction of strong electron donors (such as polycyclic aromatic compounds) with strong electron acceptors (such as halogen molecules) show resistivities many decades lower than those of the parent compounds. The complexes which have been most thoroughly studied are those which involve the combination of iodine with polycyclic hydrocarbons [1-3], with aromatic diamines [4, 5] and with thiazines [6, 7]. Such materials may in theory serve as satisfactory iodine electrodes in solid-state cells, since their resistivities remain low for a wide range of halogen composition [1, 2, 4, 7]. Despite this and the relative ease of preparation and stability of these complexes, investigations of their electrochemical properties are still relatively scarce. While such materials have been used as electrodes in cells having anodes of magnesium [8] and lithium [9, 10], only the overall discharge behaviour of the cells has been reported, without a detailed analysis of the performance of the charge transfer complex electrode.

Such an analysis was undertaken by one of the authors [11] for the case of the iodine-perylene (I_2 -P) complex coupled with a silver anode and silver rubidium iodide solid electrolyte ($RbAg_4I_5$).

The behaviour of the I_2 -P electrode was so encouraging in terms of stability, polarizability and reversibility that it was considered adequate for the development of silver-iodine solid-state power sources. It therefore seemed useful to investigate the behaviour of alternative iodine charge transfer complexes having comparable resistivity. One disadvantage of the I_2 -P complex is the relatively high cost of the organic component.

The present investigation has concentrated on three materials: iodine-o-tolidine (I_2 -Ot), iodine-phenothiazine (I_2 -Ph) and iodine-N-methylphenothiazine (I_2 -MePh), and we have studied both electrical and electrochemical properties.

The characteristics of a number of charge transfer complexes are summarized in Table 1. For all the complexes listed, the resistivity is found to have an exponential temperature dependence: $\rho = \rho_0 \exp(E_a/kT)$, where E_a is a constant. It is often assumed that conductivity in charge transfer complexes of this type is similar to that of an intrinsic semiconductor where electrons are promoted from a bound state to a conduction band. Under these circumstances, and if there are no vacant donor states initially, the number of charge carriers is proportional to $\epsilon/2kT$ where ϵ is the energy interval of the band gap. Assuming that the electron mean free path is effectively temperature independent, values for the band gap can be

Table 1. Properties of iodine charge transfer complexes at 20°C

Donor, D	Composition, I ₂ /D (mole ratio)	Resistivity, ρ (Ω cm)	Activation energy, E _a (eV)	Reference
Perylene	1.5	9-10	0.03	(2)
	3.0	9-10	0.03	(2)
	1.5	8	0.02	(3)
Pyrene	2	75	0.07-0.14	(3)
Violanthrene	4	45	0.07	(1)
Benzidine	1.00	620	0.19	(4)
	1.25	2.2	0.19	(4)
	1.50	12	0.19	(4)
	1.50	200	—	(5)
O-tolidine	1.00	290	0.24	(4)
	1.25	29	0.18	(4)
	1.50	91	0.18	(4)
Phenothiazine	1.5	20	0.17	(6)
	1.5	350	—	(7)
N-methylphenothiazine	1.5	1.4	0.14	(6)

determined by equating the experimental constant E_a with $e/2$.

2. Experimental

O-tolidine, phenothiazine and iodine were reagent grade products. Complexes formed using sublimed phenothiazine were also investigated. N-methyl phenothiazine was prepared by reaction of excess methyl iodide with phenothiazine and sodium in hexamethylphosphotriamide after the method of Normant *et al.* [12]. Complexes were obtained by precipitation on mixing of the two components in appropriate quantities in solutions of methylene chloride. C, H and N analyses were carried out, and the iodine content was determined by titration with standard aqueous sodium thiosulphate of the complex dissolved in benzene or acetone. Silver rubidium iodide was prepared by the standard method of melting a mixture of AgI and RbI in a 4:1 molar ratio, quenching the melt and annealing the resulting product at 160°C for over 20 h.

The formation of the complexes was studied by differential thermal analyses and resistivity measurements. The former were performed using a differential calorimeter (Perkin Elmer, Model DSC 1B). Resistivities of compressed pellets sandwiched between graphite discs were determined using an audio frequency impedance bridge. Temperature dependence of the resistivity was

investigated by enclosing the pellet of complex with associated graphite electrodes in a Teflon cell contained in a jacket, through which liquid was circulated from a thermostatic bath.

Electrochemical measurements were carried out in solid-state cells of the type:



where I₂-D is the charge transfer complex. The cells were formed by pressing the RbAg₄I₅ electrolyte and a thin layer of the complex into a single pellet. This was then held in contact with a mixture of silver and electrolyte, in a weight ratio of 1:2, which acted as the other electrode. The cell was housed in a plastic container having a gold or copper contact for the silver electrode and a graphite contact for the charge transfer complex. The container also had an opening to permit the exit of a silver wire which, inserted into the electrolyte, served as a reference electrode for the polarization studies.

3. Results and discussion

3.1. Composition of the complexes

It is not clear from the published data on the materials under investigation whether they have fixed compositions in the solid state or an infinitely variable ratio of organic electron donor to iodine. Thus, Gutmann and Keyzer [7] give a plot

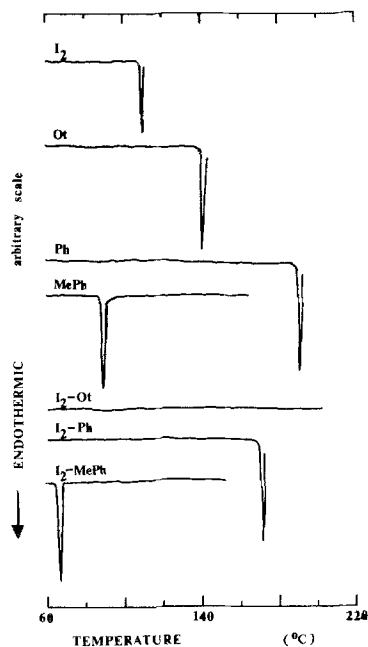


Fig. 1. Differential thermal analysis patterns (schematic).

of resistivity of phenothiazine/iodine 'complexes' ranging in composition from 2:1 to 1:6. Similarly Kusakawa and Nishizaki [4] refer to o-tolidine/iodine complexes in the ratios 1.33:1 to 1:1.5. Matsunaga [6] on the other hand, reported a fixed

composition of 1:1.5 for phenothiazine, N-methylphenothiazine, and two benzophenothiazine complexes. We prepared complexes by mixing solutions containing electron donor and iodine in a range of ratios from 1:1 to 1:2. For a starting ratio in solution between 1:1 and 1:1.27 a unique o-tolidine/iodine solid complex of composition ot (I_2)_{1.27} was formed. Similarly for solution compositions between 1:1 and 1:1.5 unique phenothiazine/iodine and N-methylphenothiazine/iodine solid complexes were precipitated with compositions Ph (I_2)_{1.5} and MePh (I_2)_{1.5} respectively. The three complexes thus formed melted sharply and as shown in Fig. 1; there are no traces of starting material peaks in the differential thermal analysis traces. When the iodine component in the starting solutions was higher than the above values, however, the solid complexes were found by analysis to contain a higher proportion of iodine. These latter materials were unstable (giving off iodine) and melted over a wider range than the 'normal' complexes. It may be noted that the maximum conductivity found for Ot/ I_2 [4] and for Ph/ I_2 [7] by previous workers occurred at molar ratios corresponding with the composition of the complexes reported here.

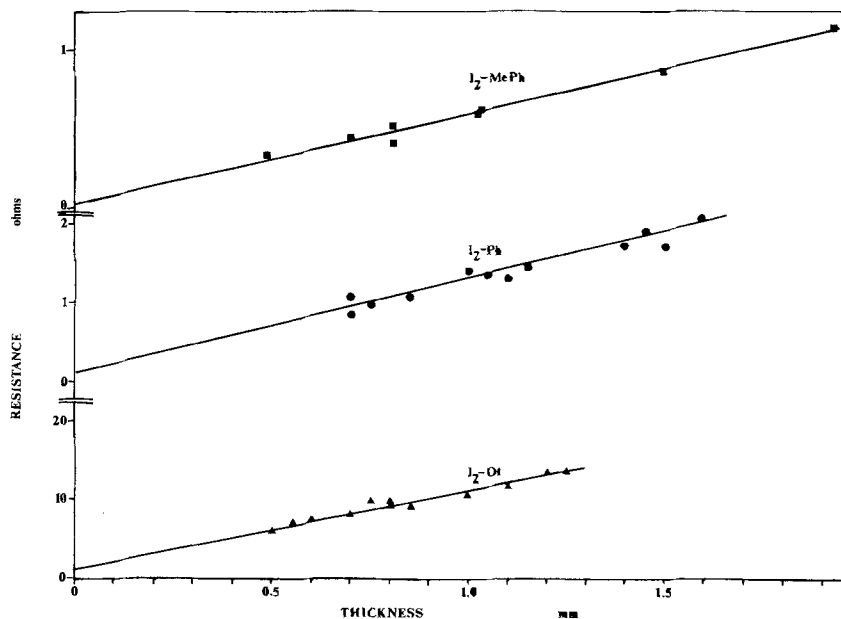


Fig. 2. Resistance determination at 25°C.

Table 2. Properties of I_2 -Ot, I_2 -Ph and I_2 -MePh at 25°C

Complex	Composition I_2/D (mole ratio)	Resistivity (Ω cm)	Activation energy (eV)
I_2 -Ot	1.27	136 ± 13	0.18
I_2 -Ph	1.5	16 ± 1	0.12
I_2 -MePh	1.5	4.4 ± 0.5	0.15

3.2. Electrical measurements

For the measurement of resistivity, graphite pellets were used as contacts since gold electrodes react with the complexes, thus substantially increasing the interfacial resistance. This effect was also noted by Kusakawa and Nishizaki [4]. Contact resistances were found by extrapolating resistance versus sample thickness plots as shown in Fig. 2, and varied from 0.04 Ω for I_2 -MePh to approximately 1 Ω for I_2 -Ot. The resistivities of the three complexes are given in Table 2. The value for I_2 -Ph is in good agreement with that found by Matsunaga [6] (Table 1) while the higher value found by Gutmann and Keyzer is probably due to the use of gold electrodes by those workers [7]. The resistivities of the I_2 -Ot and I_2 -MePh prepared in the present study are both slightly higher than the literature values [4, 6]. The temperature dependence of the resistivities is shown in Fig. 3. From the linear $\log \rho$ versus $1/T$ plots, the activation energies were derived and are reported in Table 2.

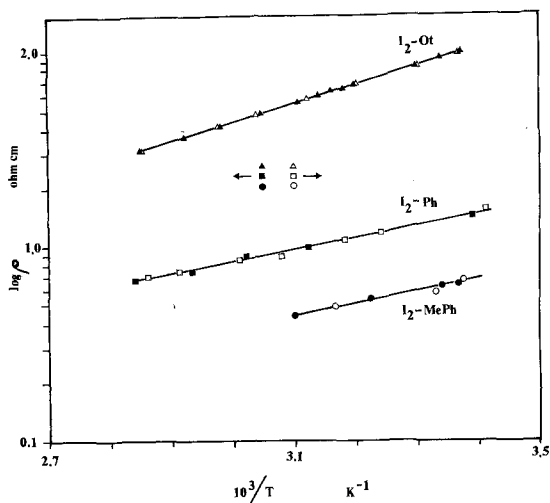
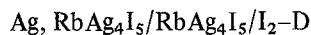


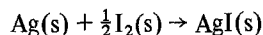
Fig. 3. Temperature dependence of the resistivity.

3.3. Electrochemical measurements.

Cells of type (I)



were assembled, (where I_2 -D was one of the three charge transfer complexes of fixed composition under investigation) and emf's were measured. Values of the emf's at 25°C are given in Table 3. Considering that the cell process



has an emf of 0.690 V at this temperature, one may associate the observed differences in potential with the free energy of dissociation of the iodine complexes. Since the diffusion of iodine in the cathode is likely to be hindered by strong bonding to the organic substrate, one might predict that under the passage of current mass-transfer polarization would occur at lower current densities for complexes with higher dissociation energies. This is indeed found to be the case, as shown by the polarization curves of the iodine electrodes of the cells, reported in Fig. 4. The low mass-transport controlled current of the I_2 -Ot complex compared with that of the other two complexes indicated its limitation as a practical iodine electrode system, and attention was therefore concentrated on I_2 -Ph and I_2 -MePh.

Table 3. Emf of cells $\text{Ag, RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/I_2-D^*$

Complex	Composition I_2/D	emf
I_2 -Ot	1.27	0.58
I_2 -Ph	1.50	0.63
I_2 -MePh	1.50	0.64

*Note: Unstable open circuit voltages were found for cells having I_2 -D electrodes with higher I_2 ratios.

Typical discharge curves are shown in Fig. 5 for cells of type I where D was I_2 -Ph and I_2 -MePh. The shapes of the curves and the percentage cathode capacity attained, of the order of 90%, were satisfactory and comparable with the results obtained for similar cells using I_2 -perylene as cathode [11]: i.e. the resistivities of these complexes also remains low for a wide range of iodine composition.

To investigate the rechargeability of the charge-

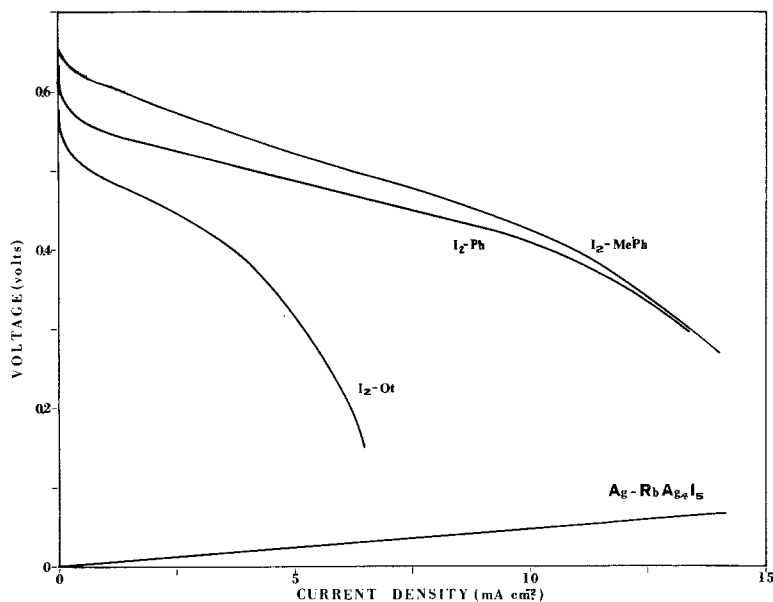


Fig. 4. Electrode polarisation curves of cell I at 25°C.

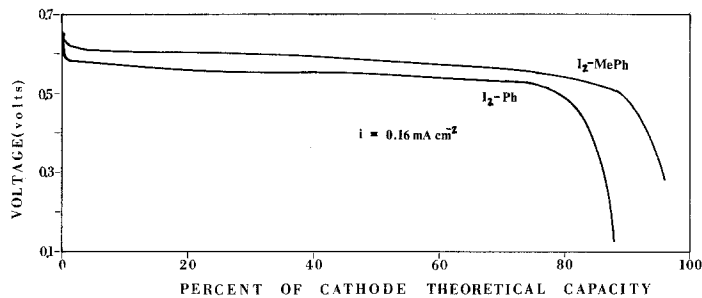


Fig. 5. Discharge curves at 0.16 mA cm^{-2} for $\text{I}_2\text{-MePh}$ and $\text{I}_2\text{-Ph}$ in cell I at 25°C.

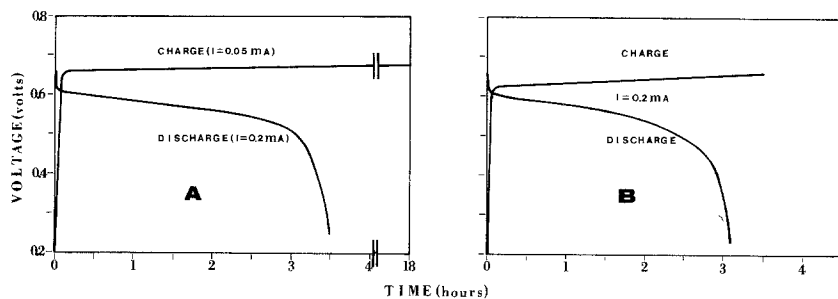


Fig. 6. Typical charge/discharge cycles for $\text{I}_2\text{-Ph}$ in cell II at 25°C. (a) first cycle; (b) second cycle.

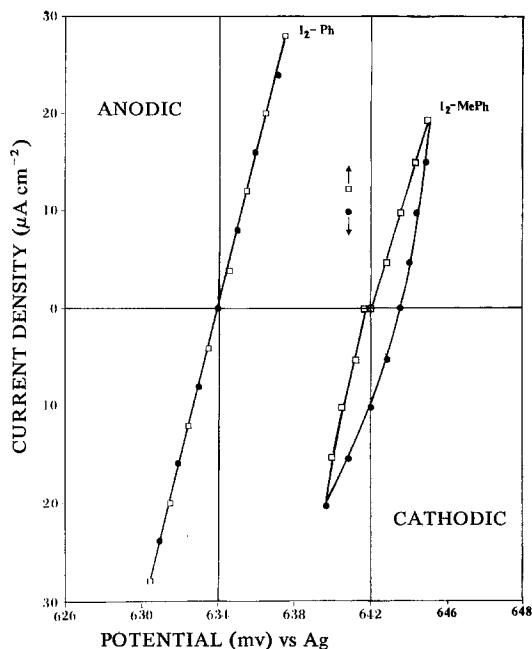
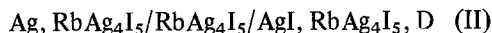


Fig. 7. Micropolarization of I_2 -Ph and I_2 -MePh electrodes.

transfer complex iodine electrodes, cells of the type



the fully discharged versions of cell (I) were assembled and submitted to charge. In the mixture forming the positive electrode of the above cell, AgI and D were in such proportions to assure the formation of I_2 -D complexes of 1.5:1 molar ratio after a complete electrochemical conversion of silver iodide into silver and iodine. Silver rubidium iodide was added to reduce interfacial polarization effects. A thin layer of this mixture was pressed onto the electrolyte to form a single pellet, which was then placed in contact with a pellet of Ag and RbAg_4I_5 mixture.

After charging at approximately 0.05 mA cm^{-2} until 80% complete conversion, the cell based on phenothiazine displayed a stable open circuit voltage of 0.630 V. Subsequent discharge of the cell at 0.2 mA cm^{-2} gave an efficiency of 78%. In a second charge/discharge cycle the efficiency rose to 85%. These cycles are shown in Fig. 6. In the case of N-methylphenothiazine, however, the charge/discharge efficiencies were inferior,

being approximately 55% for the first cycle and 83% for the second. This would seem to indicate a lower degree of reversibility for the I_2 -MePh electrode in comparison with the I_2 -Ph system. This hypothesis is confirmed by the respective micropolarisation curves shown in Fig. 7.

4. Conclusion

On the basis of the above results, it may be concluded that the I_2 -Ph and I_2 -MePh complexes offer excellent prospects for use as iodine electrodes in solid-state cells. The electrodes show excellent discharge capabilities, are rechargeable and thus may be prepared electrochemically, and present the important commercial advantage of being of low cost compared with other iodine charge transfer complexes.

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References

- [1] H. Akamatu, H. Inokuchi and T. Matsunaga, *Bull. Chem. Soc. Japan* **29** (1956) 213.
- [2] T. Uchida and H. Akamatu, *ibid* **34** (1961) 1015.
- [3] J. Kommandeur and F. R. Hall, *J. Chem. Phys.* **34** (1961) 129.
- [4] H. Kusakawa and S. Nishizaki, *Bull. Chem. Soc. Japan* **38** (1965) 313.
- [5] J. A. van der Hock, J. H. Lupinski and L. A. Oosterhoff, *Mol. Phys.* **3** (1960) 299.
- [6] Y. Matsunaga, *Helv. Phys. Acta* **36** (1963) 800.
- [7] F. Gutmann and H. Keyzer, *J. Chem. Phys.* **46** (1967) 1969.
- [8] F. Gutmann, A. M. Hermann and A. Rembaum, *J. Electrochem. Soc.* **114** (1967) 233.
- [9] B. Scrosati and M. Torrioni, *Electrochim. Acta* **18** (1973) 225.
- [10] A. A. Schneider, W. Greatbatch and R. Mead, 9th International Power Sources Symposium, Brighton, UK, 1974, abstr. 30.
- [11] B. Scrosati, M. Torrioni and A. D. Butherus, 'Power Sources 4' p. 453, Oriel Press, 1973.
- [12] H. Normant, T. Cuvigny, J. Normant and B. Angelo, *Bull. Soc. Chim. de France* (1965) 3446.