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The parathiocyanogen electrode

Abstract Stable, yellow anodic films of parathiocyanogen $(SCN)_x$ were formed on a platinum electrode from 2.8 M KSCN in methanol at 45 °C at a constant current of 20–40 mA cm^{-2} for 15–30 min. Loosely bound orange crystals of a more amorphous character were removed by rinsing to leave an adherent yellow film with sharp Raman bands under 647.1 nm laser excitation at 627 cm^{-1} (vCS), 1152 cm^{-1} and 1236–1261 cm^{-1} (vNN and vCN). The lack of electroactivity and short-lived photocurrents pointed to an insulating film at potentials up to 1.0 V (SHE). At more positive potentials, longer-lasting photocurrents were obtained, consistent with breakdown of the insulating film. XPS scans confirmed N:C:S ratios close to 1:1:1, with a deficiency of S of some 10% due to S lost as sulfate at the film surface. Oxidation of SeCN$^-$ in neutral aqueous solution led to the formation of a less-stable orange paraselenocyanogen film with a Raman band at 1256–1267 cm^{-1}, which decomposed within a day to grey selenium.

Key words Parathiocyanogen · Conductivity · Photoelectrochemistry · Raman spectroscopy

Introduction

The oxidation of thiocyanate at an inert metal electrode has long been known to produce a variety of soluble products in aqueous solutions, such as SO_4^{2-}, CN^-, CO_3^{2-}, NO_2^-, and the trithiocyanate ion $(SCN)_3^-$ [1–4].

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The oxidation of thiocyanate on an inert electrode is in fact known to lead initially to the formation of thiocyanogen [1–3, 5, 6]:

$$2SCN^- \rightarrow (SCN)_2 + 2e^- \quad E° = +0.77\,V \quad (1)$$
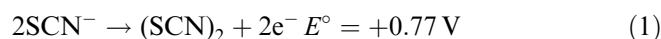
Thiocyanogen has been shown to have Raman bands at 489 cm^{-1} (vS—S), 668 cm^{-1} (vC — S) and 2160 cm^{-1} (vC ≡ N) [3, 5, 7], and has been assigned the structure N ≡ C — S — S — C ≡ N. However, thiocyanogen is stable only at lower temperatures and in nonaqueous solvents such as methanol or acetic acid, while in aqueous solutions thiocyanogen is readily hydrolysed to produce solution species.

At the same time, a yellow or orange-red precipitate named parathiocyanogen or pseudothiocyanogen, $(SCN)_x$, has been observed to form on an inert electrode [1, 4, 6, 8]. The formation of parathiocyanogen is favoured at higher temperatures in nonaqueous solutions. For example, Martinez et al. [6] observed the formation of a yellow-orange film on Pt in 2 M KSCN in DMSO at 157 °C, which passivated the electrode at an average thickness of 4 μm. These same researchers used the formation of parathiocyanogen on Pt in solutions of KSCN in acetonitrile at 76 °C as an example of the mechanism of film formation under ohmic resistance control [8]. In another study the mass spectrum taken of the compound was fitted with the formula $C_6N_6S_4$ [1].
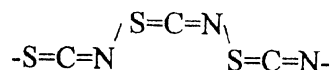
A yellow electrode film of parathiocyanogen has also been formed from thiocyanate melts. While this film was ascribed to a layer of sulfur in some early cases [9], microprobe analysis pointed to C, N and S present in a 1:1:1 ratio consistent with parathiocyanogen formation [10]. The deposit formed on a variety of substrates was also found to be photoelectrically active, generating an anodic photocurrent [9, 11, 12]. The production of parathiocyanogen was favoured at a high temperature and high current density, while under other conditions the trithiocyanate ion and its own polymer were formed [12]. A broad IR band between 1100 and 1300 cm^{-1} was seen for parathiocyanogen with at least three peaks at 1140, 1210 and 1260 cm^{-1} [12].

More recently, Cataldo [13, 14] has optimised the procedure for forming parathiocyanogen both chemically and electrochemically using concentrated methanolic thiocyanate solutions at 45 °C. Large quantities of yellow parathiocyanogen powder were dislodged from the platinum electrode using an ultrasonic bath, while thin films of the polymer were also formed on the electrode but were not studied further.

Cataldo found that the conductivity of compressed pellets of parathiocyanogen powder increased upon doping with iodine, from about 7×10^{-10} S cm^{-1} initially, to 2×10^{-6} S cm^{-1} after 4 days, and 1.2×10^{-4} S cm^{-1} after 7 days exposure to iodine [14]. A comparison is then possible with similar polymeric systems such as poly(sulfur nitride), which becomes even more highly conducting upon doping. However, this conductivity is well short of that of conducting polymers such as polyaniline or polypyrrole, which are of the order of 10–100 S cm^{-1}, and so parathiocyanogen was described as a "high resistive semiconductor". ESR studies of parathiocyanogen also pointed to the presence of a large number of unpaired spins [14]. Two maxima were seen in the UV spectra at 267 nm and 440 nm, the latter ascribed to the presence of conjugation and delocalised electrons along the polymer chains.

The IR spectrum of parathiocyanogen was compared with those of NaSCN, Na(SCN)$_3$ and a triazine-based model compound [13]. The IR spectrum of parathiocyanogen showed a very strong and broad band centred at 1220 cm^{-1} which was ascribed to S — N stretching with a bond order between the S and N atoms of around 1.5, superimposed on the absorption in the same region of the S — C stretching of S — C bonds with the same 1.5 bond order. A shoulder at 1520 cm^{-1} was assigned to a = C = N —conjugated system, and the band at 600 cm^{-1} to νC — S. Parathiocyanogen powder formed by electrochemical means showed the same IR spectra, and hence the same structure, as chemically prepared parathiocyanogen [14]. The structure of parathiocyanogen differed from that of the triazine compound and from (SCN)$_3^-$, and the following formula was suggested [13]:

$$\text{-S=C=N} \underset{\diagdown}{\overset{\diagup \text{S=C=N} \diagdown}{}} \text{S=C=N-}$$

In the present research the focus has been placed upon the film of parathiocyanogen formed electrochemically on a platinum electrode, using the method of Cataldo, but without removing the film. The parathiocyanogen film was studied using cyclic voltammetry and the photocurrent response on a millisecond timescale to a brief, intense light-flash [15, 16]. The polymeric film was also studied using ex situ Raman, IR and X-ray photoelectron spectroscopy (XPS).

Experimental

Solutions were made up using methanol (UV grade, AJAX Chemicals) or Milli-Q grade water, while KSCN, KSeCN and other chemicals were of AR grade and were used without further purification. The working electrode was a platinum disc (0.28 cm^2), formed by mounting a 6 mm diameter piece of 0.125 mm thick platinum foil (99.99% pure, supplied by Advent Research Materials), on the end of a stainless steel shaft set in a Teflon holder. A platinum loop 50 mm in diameter served as the counter electrode, and a saturated calomel electrode as the reference electrode (242 mV). All potentials reported here are relative to the standard hydrogen electrode (SHE) scale. Electrochemical experiments were conducted using a PAR 173 Potentiostat with a PAR 276 Interface Module driven by PAR 270 Electrochemical Research Software. To prepare samples for XPS, a 1.7 cm^2 square piece of 0.125 mm thick platinum foil was used as the working electrode. A small hole was punched in one corner of the platinum square to allow it to be suspended from a platinum wire shaped as a hook, with the hook kept just out of the solution.

The photocurrent responses of the films to a brief, intense light-flash from a conventional camera flash unit were recorded using a PicoScope ADC-100 analog-to-digital converter with PicoScope software, taking 42 points per millisecond (see [15, 16] for more details). In earlier work it was shown that, for conducting polymers of the polyaniline family, short-lived photocurrents are observed when the polymer is in an insulating state, while much longer-lasting photocurrents are given for the polymer in a conducting state [15].

The Raman spectra were taken ex situ using an Anaspec CARY-81 spectrometer, using a Cr-500 K krypton-ion laser at 647.1 nm, and a GaAs photomultiplier tube detector. The spectra were taken in 1 cm^{-1} steps, with 2 cm^{-1} slit width and 100 mW laser power. IR spectra of the parathiocyanogen powder in a KBr disc were obtained on a Perkin Elmer Paragon 1000 PC FTIR spectrometer. The electrode film was examined by reflectance IR spectroscopy using a Digilab FTS-60 FTIR spectrometer.

The XPS spectra were run on a Kratos XSAM800 X-ray photoelectron spectrometer, with Mg $K\alpha$ radiation (1253.6 eV) set at 18 mA and 12 kV (see [16] for more details). X-ray diffraction (XRD) scans were taken using a Philips PW 1010/30 X-ray generator with Sietronics interface unit. Scans were taken in 0.03° steps from 2 to 62° over periods ranging from 20 min to 20 h.

Results

Electrochemistry and photocurrents

Parathiocyanogen films were formed on a platinum electrode at a constant current of 20–40 mA cm^{-2} for 15–30 min in methanolic solutions of 2.8 M KSCN at 45 °C. Holding the current at 40 mA cm^{-2} led to a nearly steady potential of around 0.7 V (SHE) for some 10 min, by which time the electrode remained largely colourless with a trace of yellow-coloured solution near the Pt surface. Oxidation for longer times led to a rise in potential to about 1.0 V after 30 min. By this time the electrode surface had become covered with a yellow insulating material with a large amount of "foamy" yellow-orange crystals at the electrode surface which were poorly adherent. These orange crystals were later removed by gentle washing with ethanol to leave the more adherent yellow film. All of the films and powders were very stable, and similar Raman, IR and XPS spectra were obtained even after several weeks exposure to the air.

Parathiocyanogen films were examined in aqueous solutions of NaCl or HCl to test the electroactivity of

the film and the presence of internal redox processes. The parathiocyanogen films in fact showed little redox activity up to 1 V and behaved as a passive, insulating material; increasing anodic currents were only obtained at more positive potentials.

For parathiocyanogen exposed to potentials no greater than 1 V (SHE), only short-lived photocurrents were obtained, with time constants of about half a millisecond, (Fig. 1, Table 1). These photocurrents lasted no longer than the duration of light from the camera flash-unit and peaked at 0.2 ms, the point at which the flash is expected to show peak intensity. This result again pointed to an insulating film, in which the passage of charge carriers was severely restricted. The amount of charge passed under the most intense photocurrent at 0.9 V over the 9 ms following the photoflash was just 6 μC cm^{-2}. The observed photocurrents arose as a result of anodic reactions at the film-solution interface, leaving a negative charge at this interface which was balanced by a positive charge created at the metal-film interface, and giving rise to anodic photocurrents of a "capacitive" type, as described for polyaniline in the insulating state [15].

However, when the film was exposed to more positive potentials, the photocurrents progressively increased in duration, indicating an increase in conductivity. This is analogous to the conductivity increase observed upon doping the films chemically with iodine for more extended periods of time [14]. For a film cycled to 1.5 V,
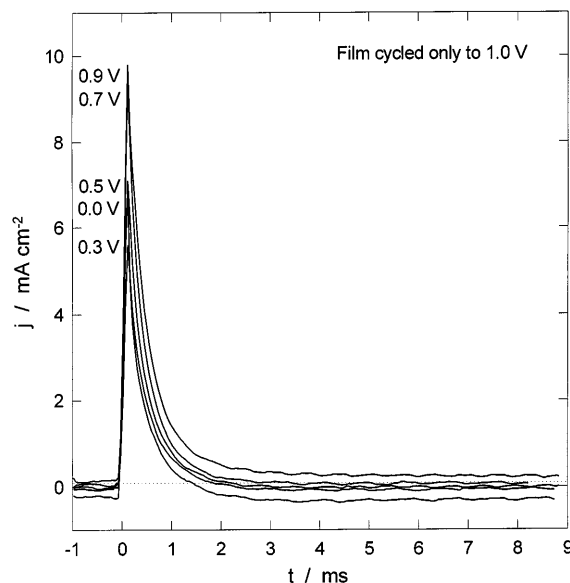

Fig. 1 Photocurrents for a parathiocyanogen film formed on a Pt electrode, and tested in 0.1 M HCl. The film had previously been cycled only to 1.0 V. The potential at which each transient was measured is given in V (SHE) on each curve

the photocurrents decayed with a time constant of 1–2 ms (Fig. 2, Table 1). Charge carriers produced in response to the light flash, such as electrons and positive holes, now outlived the light flash. While they were held

Table 1 Details of photocurrents for films of parathiocyanogen formed on a Pt electrode, and tested in 0.1 M HCl or 0.1 M NaCl, for films exposed to different oxidising potentials. Photocurrent maxima (μA cm^{-2}) and time constants for exponential decay (ms – in parentheses) are given

E (V) (SHE)	Cycled to 1.0 V 0.1 M HCl	Cycled to 1.5 V 0.1 M NaCl	Cycled to 2.0 V 0.1 M NaCl	
			after 2.0 V	after −0.5 V
−0.3		−560 (0.8)		
−0.15		−1010 (1.0)		
0.0	+6800 (0.4)	−240	−2670 (3.1)	−180 (3.3)
0.1	+6500 (0.6)	+120[a]		
0.2		+880 (1.6)		
0.3	+5600 (0.5)			
0.4		+3190 (1.3)		
0.5	+7100 (0.5)			
0.6		+3530 (1.7)		
0.7	+9300 (0.5)			
0.8		+4500 (1.8)		
0.9	+9800 (0.6)			
1.0		+4890 (2.2)	+4590 (6.1)	+5340 (5.3)
1.2		+7020 (5.0)		

[a] Anodic photocurrent following a shorter-lived cathodic photocurrent
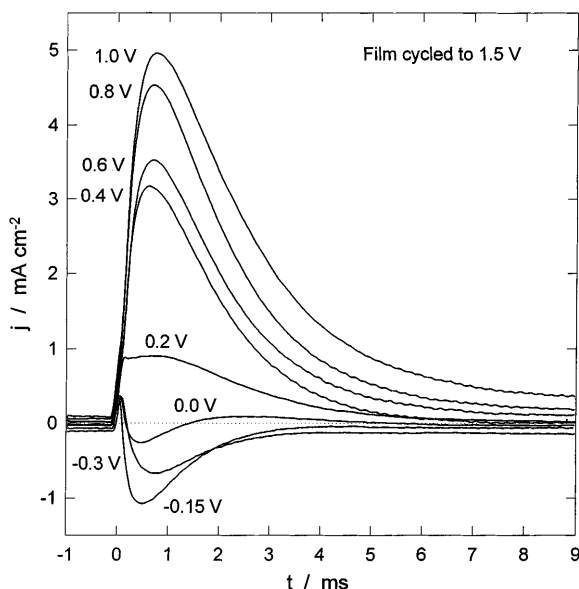
Fig. 2 Photocurrents for a parathiocyanogen film formed on a Pt electrode, and tested in 0.1 M NaCl. The film had previously been cycled to 1.5 V. The potential at which each transient was measured is given in V (SHE) on each curve

up in traps within the polymer film, they could pass more readily through the film, which was now partially conducting, leading to longer-lasting photocurrents.

Photocurrents of several milliseconds in duration were obtained for films cycled to 2 V, as more charge carriers succeeded in passing through the film to carry the current (Fig. 3, Table 1). A comparable photore-
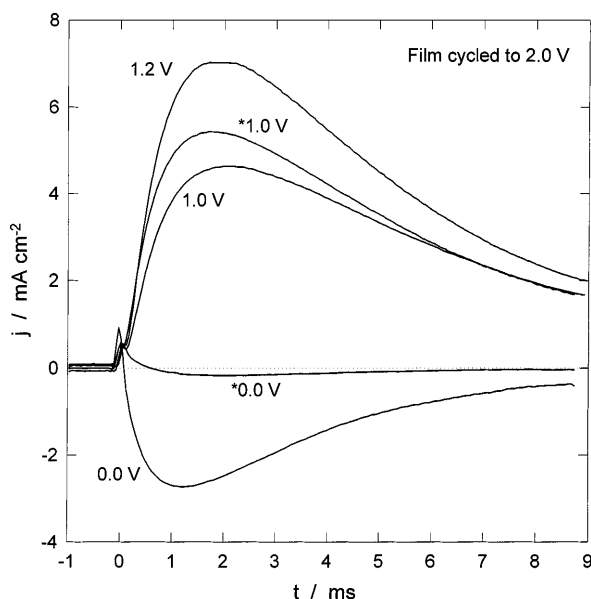

Fig. 3 Photocurrents for a parathiocyanogen film formed on a Pt electrode, and tested in 0.1 M NaCl. The film had previously been cycled to 2.0 V. The potential at which each transient was measured is given in V (SHE) on each curve; * after holding the potential at −0.5 V

sponse with a lifetime of about 30 ms had been previously reported by Pucciarelli et al. [12] for para-thiocyanogen formed from KSCN melts (at quite high voltages) when exposed to a flash lamp. The charge under the first photocurrent curve at 1.0 V was now 29 μC cm^{-2} over the 9 ms after the flash, a value several times that obtained for the parathiocyanogen film which had experienced potentials no greater than 1.0 V.

Moreover, when the films were then exposed to a reducing potential at −0.5 V, the photocurrents at 1 V did not decrease in duration (see the similar photocurrent obtained for the film treated firstly at 2 V and then under reducing conditions at −0.5 V, in Fig. 3). This result contrasts with conducting polymers such as polyaniline and polypyrrole, where the partially oxidised and conductive state is readily lost upon reduction of the film, and short-lived photocurrents are regained. With parathiocyanogen the effects of oxidation were irreversible; the doped film could not be later undoped. It is likely that the oxidation reaction represents a degradation of the parathiocyanogen film. As a result conduction paths are opened up through the film to the electrode as the material is broken down. In this state, charge carriers formed as a result of the photoflash can make their way to the electrode (with their lifetime increased by numerous trapping states along the way), leading to a longer-lasting photoresponse. The diminution of the photocurrent at 0 V after reduction at −0.5 V indicates that the cathodic photocurrent prior to reductive treatment was linked to some reducible material in the oxidised film.

Raman and IR spectroscopy

Some differences in the Raman spectra were seen between an unwashed parathiocyanogen film and a film which had been rinsed with ethanol (Fig. 4, Table 2). The film which had not been rinsed with ethanol retained a mass of loosely held orange crystals on top of the more adherent yellow film beneath. The yellow adherent film gave sharp Raman bands at 627 cm^{-1} (possibly due to carbon-sulfur stretching vibrations), and at 1152 and 1236 cm^{-1}. When the orange crystals were left on the film (presumably the parathiocyanogen powder examined by Cataldo [13, 14]), the bands were much broader, extending well beyond the 1238 cm^{-1} peak to much higher values, suggesting a less homogenous polymeric structure, a wider range of polymer chain lengths, or some further chemical substance formed as a side-product.

Bands at 747 and 2067 cm^{-1} due to residual thiocyanate amidst the orange crystals could also be seen, and once the film was rinsed in any way these bands disappeared as the soluble thiocyanate was washed away. A band ascribed to sulfate ions was seen at 981 cm^{-1} with the yellow adherent film after washing with ethanol. This band was not seen while the orange crystals remained on
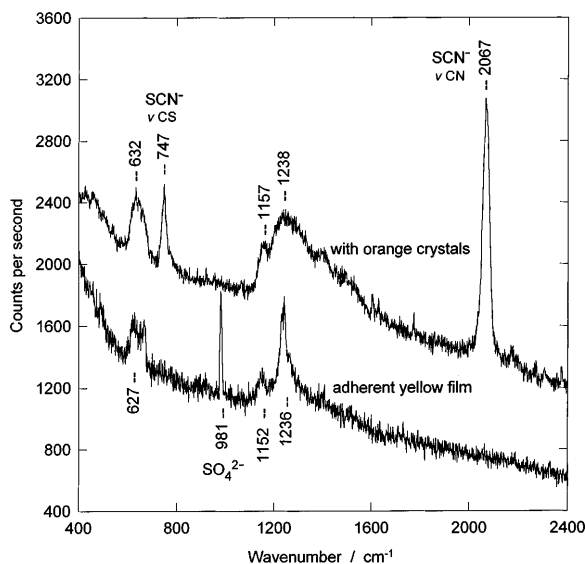
Fig. 4 Raman spectra of a parathiocyanogen film formed on a Pt electrode and tested ex situ, before (while orange crystals remained) and after rinsing with ethanol (leaving just the adherent yellow film). Laser: Kr^+ 647.1 nm
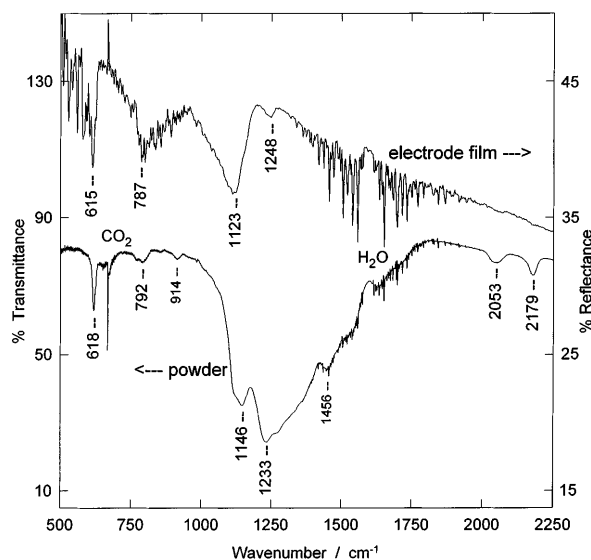

Fig. 5 IR spectrum of parathiocyanogen powder dried overnight in a desiccator, and pressed into a KBr disc (8 scans at 1 cm^{-1} resolution). Reflectance IR spectrum taken ex situ of a parathiocyanogen film on Pt

the electrode, and also disappeared when the film was subsequently washed with distilled water, showing that the sulfate was not an inherent constituent of the yellow parathiocyanogen film.

IR spectra were taken both of the parathiocyanogen powder (dried in a desiccator or in an oven at 100 °C), in a KBr disc, and of the electrode film, using reflectance IR spectroscopy. IR spectra of the parathiocyanogen powder (Fig. 5, Table 2) gave a good match with the IR spectra published by Cataldo [13, 14]. A broad intense band which peaked at 1233 cm^{-1} dominated the spectrum. Further features comparable to the Raman spectra were also seen at 618 and 1146 cm^{-1}. Additional bands not seen in the Raman spectra appeared at 792 and 914 cm^{-1}. A small band was also seen at 2053 cm^{-1}, corresponding to residual SCN$^-$.

Most of these features were seen to appear in reflectance IR spectra taken of the electrode film (Fig. 5, Table 2). However, as with the Raman spectra, the band at 1248 cm^{-1} (quite low in intensity in this case) did not extend out to much higher wavenumbers as in the case of parathiocyanogen powder. This again suggested a more varied chemical composition for the powder versus the adherent yellow electrode film.

XPS and XRD

The X-ray photoelectron spectra of several films were taken to provide information on the atomic composition and oxidation states of the elements in parathiocyanogen. The results are summarised in Table 3, with narrow scans for a typical run presented in Fig. 6. The normalised relative amounts of nitrogen, carbon (excluding contaminating graphitic carbon) and sulfur for seven samples are also recorded in Table 3, along with the results for two samples of parathiocyanogen powder by chemical microanalysis of the elements.

The elemental analysis afforded by the XPS scans gave nearly equal amounts of carbon and nitrogen, once the graphitic carbon (34% of the total carbon in the case recorded in Fig. 6) was accounted for. However, the amount of sulfur was deficient by 10–25% in various samples. Microanalysis of parathiocyanogen powder also showed a deficiency of sulfur, giving a N:C:S ratio of 1:1:0.8. However, when one sample in the XPS spectrometer was subjected to sputtering for 2 min with an argon pressure of 8×10^{-8} Torr, the ratio became very close to 1:1:1, with 33.6% for each of nitrogen and sulfur and 32.8% for carbon (after accounting for the

Table 2 Raman and IR bands obtained for parathiocyanogen films and powders

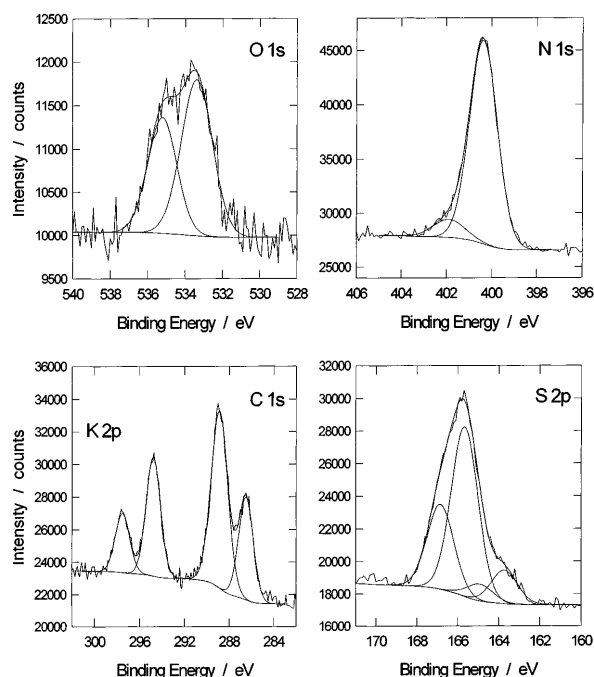| Assignment	Yellow electrode film		Orange crystals	
	Raman	IR	Raman	IR
νCS	627	615	632	618
	664	787		792
νNN (1.5 bond order)	1152 m	1123 s	1155–1162	1146 m
νCN (1.5 bond order)	1236–1261 s	1248 w	1238–1253 s	1233 s

Fig. 6 X-ray photoelectron spectrsocopy narrow scans of a para-thiocyanogen film formed on a Pt electrode in 2.8 M KSCN in methanol. The raw (unscaled) data (*jagged curve*) have been deconvoluted into Gaussian/20% Lorentzian peaks on a Shirley background with peak summations (*smooth lines*) also shown

remaining graphitic carbon). More extensive sputtering led to wildly varying values as the sputtering process severely degraded the film structure. Up to 6% potassium was also detected. Similar spectra were obtained with samples of the orange parathiocyanogen powder washed off the electrode as for the adherent para-thiocyanogen film. This further confirmed the similar chemical composition of the powder and the electrode film.

A closer look at the N $1s$ signal (in Fig. 6) showed that nitrogen existed predominantly in one chemical environment at 398.5 eV. The value of 398.5 eV is typical of nitrogen in many organic molecules, and was lower than the value of 399.6 eV obtained for nitrogen in unreacted KSCN. There was also a high binding energy tail, which ranged from 0 to 20% of the total nitrogen in different samples. This points to nitrogen in a more positive oxidation state. The potassium signal for K $2p_{3/2}$ at 292.9 eV was typical of K^+ as seen in potassium halides, but was less than the value of 294.4 eV seen in the KSCN solid tested by XPS or the value of 294.5 eV reported for KCN [17].

At the same time the S $2p$ signal was deconvoluted into a main doublet with S $2p_{3/2}$ at 163.8 eV, typical of sulfur in a neutral (zero) oxidation state, and close to the value of 164.0 eV obtained for S in a sample of KSCN. In some cases (as in Fig. 6), a lower binding energy tail was seen, indicative of sulfur in a more negative oxida-

Table 3 X-ray photoelectron spectroscopy scans for a parathiocyanogen film formed on Pt in 2.8 M KSCN in methanol at 45 °C by 20 min at 20 mA cm^{-2}, before drying overnight in a desiccator and transfer to the XPS instrument and testing on the following day (narrow scans at a take-off angle of 90°).

Wide scan	Atomic percentage (%)	Normalised (no graphitic carbon)	Normalised (av. of 7 runs with SD)	Micro-analysis[a] (% atoms)
Oxygen	4.6			
Nitrogen	25.1	35.0	**35.8** (1.4)	**35.0**
Potassium	4.6			
Carbon	39.2	36.1	**35.1** (2.5)	**36.1**
Sulfur	20.7	28.9	**29.1** (2.7)	**28.9**

Narrow scans	Orbital	Raw binding energy (eV)	Scaled binding energy (eV)	FWHM (eV)	Percentage of each element (%)
Oxygen	1 s	533.4	531.5	1.97	59.2
2 forms		535.2	533.3	1.83 H$_2$O	40.8
Nitrogen	1 s	400.4	398.5	1.44 N(0)	90.7
2 forms		401.9	400.0	1.65 N$^{(+)}$	9.3
Potassium	2p	294.8	292.9	1.51 K$^+$	100
1 doublet		297.5	295.6	1.55	
Carbon	1 s	286.5	**284.6**	1.55	34.0
2 forms		288.9	287.0	1.75 CN	66.0
Sulfur	2p	163.7	161.8	1.52 S$^{(-)}$	16.4
2 doublets		164.9	163.0	1.55	
		165.7	163.8	1.54 S(0)	83.6
		166.8	164.9	1.59	

[a] Conventional chemical analysis of the dry solid

tion state. While oxide species were also shown to be present on the film surface these were quickly removed by sputtering, showing that oxygen was not a constituent of the parathiocyanogen film.

The presence of positive nitrogen and negative sulfur points to a significant amount of charge separation in many of the films studied. Sulfur in a negative oxidation state was balanced by nitrogen in a positive oxidation state and by positively charged potassium ions in the film. At other times the amount of positively charged nitrogen and negatively charged sulfur was practically zero, including one film which had been left exposed to the air for a number of weeks. These differences may relate back to the conditions under which the films were prepared, in which the potential at times spiked well over 1 V. On these occasions the films may have been subjected in an uncontrolled manner to the oxidising conditions responsible for the processes leading to positively charged nitrogen and negatively charged sulfur.

While parathiocyanogen powders are known to be rather amorphous in character, the parathiocyanogen electrode films produced in this study were shown to be more chemically pure than the parathiocyanogen powders (given by sharper Raman bands in particular). To test the crystallinity of the electrode material and the powder, diffraction patterns were obtained in air using an X-ray diffractometer.

For a 20 h scan of the electrode film over 2–62°, only peaks at 40.07° and 46.54° due to the platinum substrate, and a peak at 21.62° due to platinum oxide, were observed. While a small feature at 24.05° was also seen and could not be assigned, no strong lines attributable to parathiocyanogen were observed, pointing to a non-crystalline structure. A 1 h scan was also taken of parathiocyanogen powder; from 15° to 45° several lines were observed due to unreacted KSCN, and an unassigned line at 23.92°.

Oxidation of selenocyanate

A comparison was also made with films formed by the oxidation of selenocyanate. $SeCN^-$ cannot be tested in acidic solutions owing to its decomposition into colloidal selenium, while selenocyanate melts are not formed owing to the decomposition of KSeCN on heating. Bragadin et al. [18, 19] achieved the high salt concentration needed to form a yellow $(SeCN)_x$ deposit by using an "ammoniate" solution (2:1 NH_3 to KSeCN, formed by passing NH_3 through the dry salt). However, apart from the electrochemical details of its formation and the potential change on irradiation, no spectral or other structural data were given.

The oxidation of selenocyanate in aqueous solutions gave a patchy orange-red film when the electrode was cycled to just 0.6 V in 0.5 M KSeCN and 0.1 M NH_4O_2CMe as a neutral pH buffer at room temperature (but not in concentrated methanol solutions). Ra-

man spectra showed bands due to grey selenium at 232 and 452–466 cm^{-1}, while a further band was observed at 1256–1267 cm^{-1}, possibly due to a paraselenocyanogen-type film. Within a day the orange colour darkened to leave grey selenium on the electrode surface, showing the instability of the paraselenocyanogen film in air.

Bands at 505 cm^{-1} and 2143 cm^{-1} due to $(SeCN)_3^-$ species appeared when a more positive oxidising potential was used (greater than 0.8 V), and these dominated reflectance IR spectra taken of the film. The assignment of these bands was confirmed by preparing a sample of $K(SeCN)_3 1/2H_2O$ according to the method of Hauge [20], modified to use dichloromethane as the organic solvent rather than benzene.

Discussion

The simplicity of the Raman and IR spectra presented above, especially the sharp bands for the more adherent yellow film at 615–632 and 1233–1261 cm^{-1} (and at 1123–1152 cm^{-1} in the IR and some Raman spectra), suggest a regular chemical structure. The parathiocyanogen powder released from the electrode appears to be more amorphous in structure, with broader Raman and IR bands, while still of the same basic structure. The results of XPS also point to sulfur, carbon and nitrogen each in a single chemical environment, with the exception of varying degrees of positively charged nitrogens and negatively charged sulfurs associated with over-oxidation of parathiocyanogen. At the same time, elemental ratios of N:C:S close to 1:1:1 were indicated from XPS scans and an elemental analysis, with a regular deficiency of sulfur by 10–20%. Bands due to soluble sulfate were also seen in the Raman spectra, possibly the end product for sulfur lost from the parathiocyanogen film near the surface. One sample subjected to light sputtering showed a N:C:S ratio much closer to 1:1:1 for lower layers of the film.

On the basis of the above results it has not been possible to determine the structure of parathiocyanogen conclusively. However, no bands due to the S — S stretching vibration were observed in the Raman spectra for parathiocyanogen in the range 400–550 cm^{-1}, as would be expected with S — S links. According to Nakamoto [21], S — S stretching bands typically lie in the 420–550 cm^{-1} region, with Feher and Weber [7] assigning bands in the 440–490 cm^{-1} region to S — S stretches for a series of $S_n(CN)_2$ compounds including thiocyanogen. Bonds between carbon and nitrogen atoms may well exist in resonance forms, giving rise to bonds of order 1.5. This may explain the strong Raman and IR bands at around 1123–1152 cm^{-1}, and at 1230–1260 cm^{-1}, possibly due to νNN and νCN bonds. The oxidation of polymer chains could give rise to unpaired spins and other defect structures. Any breaks between sulfurs and carbons along the backbone would also give

rise to charged species, giving positively charged nitrogen and negatively charged sulfur as required from the XPS results.

The formation of an anodic film from SeCN⁻ solutions, analogous to that of parathiocyanogen, was also seen in experiments run in aqueous solutions. The Raman band at 1256–1267 cm⁻¹ for the selenocyanate anodic film lay very close to the principal Raman band obtained for parathiocyanogen. If this band was due to analogous paraselenocyanogen polymeric film, the position of the band would be expected to be displaced somewhat should the relevant mode or modes involve S replaced by Se in the structure (for example, a simple calculation based on the relative reduced masses would see a NS mode at 1240 cm⁻¹ reduced to 1122 cm⁻¹ for NSe). One possible explanation is that the band at 1256–1267 cm⁻¹ is due to vibrations involving carbon and nitrogen atoms exclusively.

Regarding the conductivity of parathiocyanogen, the yellow film formed electrochemically on platinum proved to be quite electroinactive up to 1 V (SHE). Parathiocyanogen also needed a more positive potential to "dope" the film to higher conductivity than typical conducting polymers. This was shown by the presence of only short-lived photocurrents, typical of an insulating polymer, up to potentials of 1 V (SHE), with longer lasting-photocurrents produced only after exposure to more positive potentials. (In a similar way, several days of treatment with iodine were needed to raise the conductivity of parathiocyanogen significantly in the experiments of Cataldo [13, 14].)

The doping of parathiocyanogen is also quite different in character. It is not like the reversible doping of polyaniline or polypyrrole with oxidation of the conjugated backbone balanced by the insertion of balancing counter-ions. Instead the parathiocyanogen film is irreversibly degraded in part, leading to separated positive and negative portions within the polymer and the loss of sulfur as soluble sulfate. The enhanced conductivity then comes from a breakdown of the insulating film, allowing charge carriers to migrate through the film more readily. This was shown by the permanent longer-lasting photocurrents, typical of a more highly conducting polymer, formed by exposure to oxidizing potentials of 1.5–2 V (SHE), which were not lost upon reduction of the parathiocyanogen films.

If a comparison is to be made with metallic systems, the parathiocyanogen film is more like a passive and insulating oxide layer which can be ruptured in a sufficiently severe chemical environment, leading to a corroding surface which then offers little resistance to the movement of charge-carrying species.

Conclusions

Yellow anodic films of parathiocyanogen (SCN)$_x$ were formed on a platinum electrode by passing a constant current of 20–40 mA cm⁻² for 15–30 min in 2.8 M KSCN in methanol at 45 °C. Little electroactivity was seen in cycling up to 1 V (SHE), and the photocurrents in this potential range were short-lived ($\tau < 0.6$ ms), pointing to a passive, insulating material. When the potential was extended to 1.5 V and beyond, permanent longer-lasting photocurrents were obtained ($\tau = 2$–6 ms), owing to film degradation.

IR and ex situ Raman spectroscopy under 647.1 nm laser excitation giving bands (Table 2) in good agreement with the findings of Pucciarelli et al. [12] and Cataldo [13, 14]. The bands were sharper for the yellow film, while with the orange crystals the band at 1240 cm⁻¹ was very broad and extended to much higher wavenumbers, suggesting a more amorphous structure. A band at 981 cm⁻¹ due to water-soluble sulfate ions was observed with the yellow film.

XPS scans revealed ratios of N:C:S close to 1:1:1, with a slight deficiency of S (lost as sulfate) which disappeared when the outer layers of the film were sputtered away. Up to 6% potassium was also present in the films. Narrow scans over the elements revealed 0–20% of the nitrogen atoms in a positive oxidation state and from 0 to 40% of the sulfur atoms in a negative oxidation state. XRD scans, on the other hand, failed to detect lines attributable to crystalline parathiocyanogen, even for a scan lasting 20 h, pointing to an amorphous structure.

The oxidation of SeCN⁻ in aqueous solutions at potentials up to 0.6 V (SHE) led to a patchy red-orange coloured film, producing a strong Raman band at 1256–1267 cm⁻¹, suggestive the formation of an analogous paraselenocyanogen film.

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