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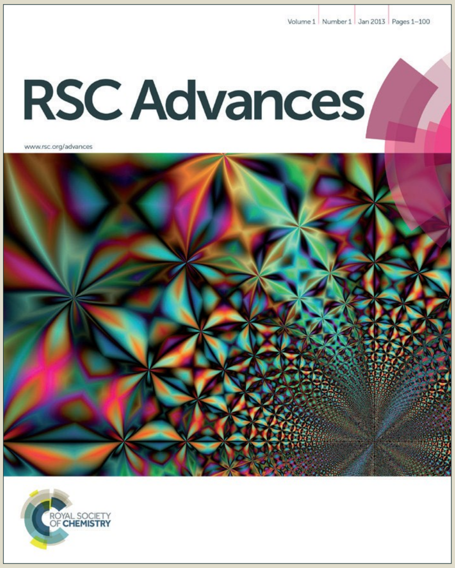

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A fundamental in situ IR spectroelectrochemical study of the electrical polarization of nickel, copper and gold electrodes in the presence of the unstable tellurocyanate ion in DMSO and DMF solutions.

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ABSTRACT

Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) studies are reported for the first time of the interaction of tellurocyanate ion ($TeCN^-$) with electrically polarised nickel (Ni), copper (Cu) and gold (Au) electrodes in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) containing tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. In general, it was conclusively shown that the $TeCN^-$ ion decomposes at certain applied potentials on electrically polarized electrochemical cells to form elemental tellurium and cyanide (CN^-) ion. The cause of the decomposition was reasoned to be due the presence of electrodissolved metal ions from the electrode which destabilise the $TeCN^-$ ion through their polarising power as cations. The severity of the destabilisation was found to

increase in the order of $Au^+ > Cu^+ > Ni^{2+}$ which is in general agreement with the relative polarising power of these metal ions. SNIFTIRS and IR transmission data from model solutions demonstrated that the metal complex ion speciation being observed during polarization experiments hence arose directly from the interaction of the metal electrode studied with CN^- ions released by decomposition rather than with the $TeCN^-$ ion itself. The potential at which electrochemical decomposition of the $TeCN^-$ ion occurred and its rate of decomposition depended on the type of metal electrode used. In general the instability of the $TeCN^-$ ion in electrochemically polarized systems reflects its fundamental chemistry of decomposing in the presence of polarizing cations and may be of use as a sensor for these species in an electrochemical setting.

INTRODUCTION:

In systems of electrochemical interest, elements such as Te and Se, for instance, have attracted much interest in their role as electrode surface modifiers and the effects they have on the electrochemical behaviour of adsorbates of relevance. For instance Te-modified single crystal Pt(111) electrodes have been studied with respect to CO adsorption and oxidation. When present as an adatom on the surface the Te was found not to catalyse CO oxidation because the adatom always existed in its reduced form on the electrode and hence could not transfer oxygen to effect the oxidation [1]. This was found to be of use in inhibiting poisoning and accumulation caused by adsorbed CO in systems where formic acid was being oxidised, particularly at intermediate coverages of the adatom[2, 3] In other studies, technologically valuable films such as cadmium telluride thin films have been prepared by electrodeposition of Te on an Au electrode followed by reduction with metal ion present[4]. Broadening the knowledge base of electrochemical processes involving tellurium based species is hence valuable for understanding their electrochemical behaviour especially if the traditional voltammetry techniques used can be combined with a spectroscopic method (e.g. infrared spectroscopy) for visualising actual molecular species. We have chosen the $TeCN^-$ ion in this study because it allows facile monitoring by IR spectroscopy due to the ν(CN) stretching vibration being in an area of the IR spectrum (2500-1800 cm^{-1}) which is uncrowded by fundamental IR vibrations. It is also a species which has not been studied previously by IR spectroelectrochemical methods but for which, the analogues of this ion, i.e. related pseudohalide ions of cyanate (NCO^-), thiocyanate (NCS^-) and selenocyanate ($NCSe^-$) have been subjected to previous IR spectroelectrochemical investigations in aqueous and polar aprotic solvents[5-7].

The successful preparation of the $TeCN^-$ ion, an inherently unstable ion, was reported in 1968 by Downs[8] who prepared it from the reaction of tetraethylammonium cyanide and elemental Te in DMF and isolated pale yellow crystals which were highly moisture and oxygen sensitive. A Raman spectrum of a solution of the ion showed a peak at 2080 cm^{-1}. ”Feebly polarizing” cations were necessary in the isolation of the solid salt because $TeCN^-$ ion cannot exist in a solid in the presence of more strongly polarizing cations like potassium or even cesium. Although $TeCN^-$ ion is relatively stable in DMF or acetone, the addition of water will instantly cause decomposition to elemental Te and CN^- ion[8] Austad et al.[9] isolated pure tetraphenylarsonium tellurocyanate, after the reaction of tetraphenylarsonium cyanide and tellurium powder in acetonitrile solution. It was demonstrated that the tetraphenylarsonium salt of tellurocyanate was reasonably stable on storage as long as no solvent traces were left on the pale yellow crystals formed. Austad et al. also published ultraviolet (UV) and infrared (IR) data for the $TeCN^-$ ion in acetonitrile and reported the ν(CN) stretching frequency of the ion at 2081 cm^{-1}. The IR stretching frequencies for the -TeCN group in solid tetramethylammonium tellurocyanate ($(CH_3)_4NTeCN$) and tetraphenylarsoniumtellurocyanate ($(C_6H_5)_4AsTeCN$) were reported in 1972 by Ellestad et al.[10] Spencer et.al.[11] reported the first preparation of $TeCN^-$ ion in DMSO and described its use in organic reactions to produce stable benzyl tellurocyanates. This and other aspects of its use in inorganic chemistry have been discussed further by Al-Rubaie et al.[12] Klaeboe et al.[13] stated that the Te-C bond is very weak which explains why it can only be isolated as a salt of large non-polarising cations like the tetraethylammonium ion or tetraphenylarsonium ion.

As the $TeCN^-$ ion is stable in only a limited range of non-aqueous solvents, the number of electrochemical studies reported which involve this ion as an electroactive species has been few. For instance, Cauquis et al.[14] reported a voltammetric study in 1975 in which the electrochemical oxidation of $TeCN^-$ in acetonitrile at a platinum microelectrode was discussed and compared with the electrochemistry of other structurally related pseudohalide ions, i.e. NCO, NCS^- and $NCSe^-$ ions. Using fast sweep rates, they were able to detect the electrochemical oxidation of $TeCN^-$ ion via a series of reactions where formation of “tellurocyanogen”, $(TeCN)_2$ was proposed to form from the combination of two tellurocyanate free radical species. The $(TeCN)_2$ species so formed was then thought to react further with more $TeCN^-$ to form the $(TeCN)_3^-$ ion. This $(TeCN)_3^-$ species (with a formal Te oxidation state of -1.33 assuming even distribution of the negative charge over the Te atoms) was then postulated to oxidise to reform $(TeCN)_2$ (with a formal Te oxidation state of -1) The $(TeCN)_2$ species is then said to subsequently decompose to form elemental Te and a cyanogen ($(CN)_2$) species. It was found that fast sweep rates minimized the importance of the decomposition of the ion to elemental Te and

$(CN)_2$ species. Cauquis et al.[14] had commented on how the instability of the $TeCN^-$ ion can cause challenges in the electrochemical detection of such transitory species.

Recently we have applied in situ IR methods such as subtractively normalised interfacial Fourier transform infrared spectroscopy (SNIFTIRS) to the study of Ni and Au electrodes anodically polarized in the presence of DMSO and DMF electrolytes containing the structurally related pseudohalide ions of NCO^-, NCS^- and $NCSe^-$.[5, 6] These studies indicated that complex ion species arising from the interaction of electrogenerated Ni(II) and Au(I) ions with the NCO^-, NCS^- and $NCSe^-$ ions in the electrolyte were formed. As $TeCN^-$ ion is fortuitously stable when prepared in dry DMSO and DMF solvents, it was decided to extend the previous work reported earlier[8, 9, 11] and study by SNIFTIRS Ni, Cu and Au electrodes electrically polarized in the presence of the $TeCN^-$ ion to 1) provide information in an area where there is a complete dearth of previous scientific investigation and also 2) to compare the electrochemistry of the $TeCN^-$ ion with that of its structurally related, more stable, analogue ions. It was also of interest to investigate whether the electrochemical behaviour of $TeCN^-$ ion as reported by Cauquis et al.[14] would occur also on these metal electrodes, and whether intermediate species such as $[TeCN]_3^-$ would be detectable by IR spectroscopy as well as comparing the behaviour of $TeCN^-$ with the related pseudohalides already studied. No previous IR spectroelectrochemical studies involving the $TeCN^-$ ion have ever been reported. Hence, this study reports SNIFTIRS work coupled with voltammetric methods on the electrochemical behaviour of the $TeCN^-$ ion on electrically polarised electrodes of Ni, Cu and Au. Further work carried out as part of this study, involved the preparation of model solutions consisting of mixtures of $TeCN^-$ ion or CN^- ion with Ni(II) and Cu(II) salts to help verify species (prepared via electrochemically independent means) observed in the SNIFTIRS studies.

EXPERIMENTAL SECTION:

The solvents used in the study (DMF, Ajax Finechem Pty, UNIVAR grade and DMSO, Scharlau, synthesis grade) were used without further distillation. However due to the moisture sensitivity of the $TeCN^-$ ion, both solvents were dried over activated type 3A molecular sieve pellets to remove traces of water. Before drying over molecular sieves, the solvents, DMF and DMSO are quoted in their specifications as having 0.1% and 0.15% water impurity as measured by Karl Fischer titration. All glassware was cleaned thoroughly with doubly distilled water prior to its use in experiments.

$TeCN^-$ ion was prepared following the procedure of Spencer et al.[11] An excess amount (0.40 g) of preground elemental tellurium (Aldrich Chemical Co, USA, 99.9%) was mixed with 0.163 g of potassium cyanide (KCN, (BDH, Anala-R grade) which had been pre-dried in a desiccator containing activated silica gel. 50 mL of dried DMSO or DMF were added to the mixture and heat applied (with the mixture having a N_2 gas flow from an oxygen free N_2 (OFN) cylinder supplied by BOC Gases pass over it) to a temperature of 80-90°C for 2 h to facilitate reaction. Successful reaction was indicated by the production of a pale yellow solution which was then filtered from the unreacted Te solid. An infrared (IR) spectrum of the pale yellow solution in DMF or DMSO featured a peak at 2079 cm^{-1} due to $TeCN^-$ ion.[9] The yellow solution was stored under OFN until required. The concentration of $TeCN^-$ produced was assumed to be 0.05 mol L^{-1} based on the amount of KCN added.

Electrolyte solutions for IR spectroelectrochemistry were prepared by adding solid tetrabutylammonium perchlorate (TBAP) from Aldrich Chemical Co, > 97.0% directly to the prepared ~0.05 mol L^{-1} $TeCN^-$ solution so that a concentration of 0.1 mol L^{-1} TBAP was produced. The TBAP functioned as an inert supporting electrolyte.

The thin layer spectroelectrochemical cell, windows, specular reflectance unit and electrodes (working, reference and secondary) used in this study were as described and illustrated in a recent publication.[5] The IR window used in the cell was a 32 x 3 mm CaF_2 window. The angle of incidence at the electrode surface was effectively 30° due to the use of the FT-30 Spectra-Tech Specular Reflectance Unit on which the cell was placed. Due to the configuration of the cell, the signals detected are due to solution species existing in the thin layer between the IR transparent window and the working electrode. The working electrode consisted of a 7 mm diameter polycrystalline Ni, Cu or Au foil electrode embedded in a glass syringe barrel using Araldite epoxy glue. The Ni electrode was from a 0.15 mm, 99.9% foil from BDH while the Au (from a 0.1 mm 99.99% foil) and the Cu (from a 0.25 mm, 99.98% foil) electrodes were purchased from Sigma Aldrich Chemical Co Ltd.

The electrochemical and spectroscopic instrumentation used to carry out the electrochemistry (CV) and IR spectroscopy of the systems were all as described in a previous publication.[5] The CV was recorded under thin layer conditions from -800 mV(AgCl/Ag) to +2000 mV(AgCl/Ag). The SNIFTIRS spectral acquisition technique involved single potential alteration as has also been described in a previous study.[5] Generally, background spectra were acquired as the average of 100 scans at -900 mV (AgCl/Ag) with all sample spectra (also the average of 100 scans) being acquired at applied potentials more anodic to this at 4 cm^{-1} resolution .

When using SNIFTIRS as the method of subtractive normalisation in the present study, the spectral configuration used led to spectra which (when containing an increasing amount of an IR absorbing species produced at an applied potential more anodic than the background potential) gave a positive going signal. Accordingly, any species existing in greater concentrations at the background potential, therefore, appeared as a negative going signal. SNIFTIRS spectra are hence displayed as + $\log_{10}(R_2(\lambda)/(R_1(\lambda))$ (R= reflectance, λ=IR wavelength, subscripts 1 and 2 refer to the reflectance of the electrode at the sampling potential and background potential respectively) rather than the opposite as has been the convention[15].

Current-potential data from the systems were collected at the same time as the IR data by averaging over 1) the starting current in the cell at the beginning of an IR acquisition and 2) the final current (after several minutes of acquisition) at the end of the scan to generate effectively what could be regarded as a “slow,” “single sweep” voltammogram of the electrode system under study.

Model solutions in the case of the Ni and Cu systems were also prepared to provide experimentally independent confirmation of the species detected and assigned in spectra acquired of the electrodes under SNIFTIRS conditions. These involved mixing partially pre-dried[16] metal salts (e.g. $CuCl_2.2H_2O$ and $Ni(NO_3)_2.6H_2O$) in DMSO along with $TeCN^-$ or CN^- ion in metal ion:$TeCN^-$ or metal ion:CN^- mole ratios ranging from 1:1 to 1:4. These model solutions were sampled by FTIR in conventional transmission mode using a Press-Lok^{TM} cell via procedures as described previously.[5]

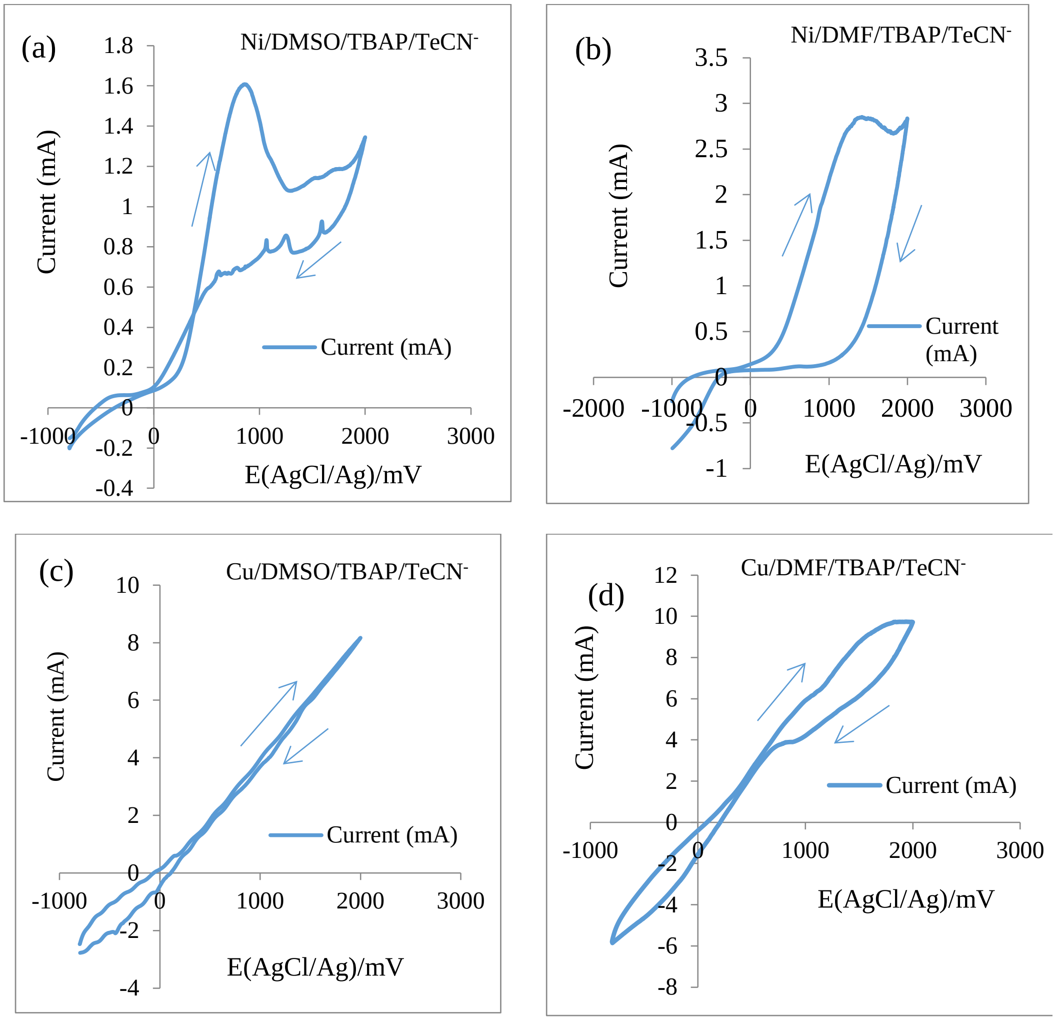
RESULTS AND DISCUSSION

1. *Cyclic voltammograms and single sweep voltammograms.*

1.1 Ni/ $TeCN^-$/TBAP/DMSO and Ni/$TeCN^-$/TBAP/DMF electrochemical systems

Figure 1(a) and (b) shows the cyclic voltammograms of the nickel electrode in $TeCN^-$/TBAP/DMSO and $TeCN^-$/TBAP/DMF based electrolytes respectively. Both CVs share the common trait of indicating a sharp increase in current in the anodic region above 0.0 mV

(AgCl/Ag) with the formation of a broad peak albeit at different values of the applied potential. CVs were recorded under thin-layer conditions. Some of the CVs (e.g. Fig 1(c) and (d)) were affected by resistance occurring in the thin layer resulting in a sharp "resistive tilt" in the appearance of the CV [17, 18]



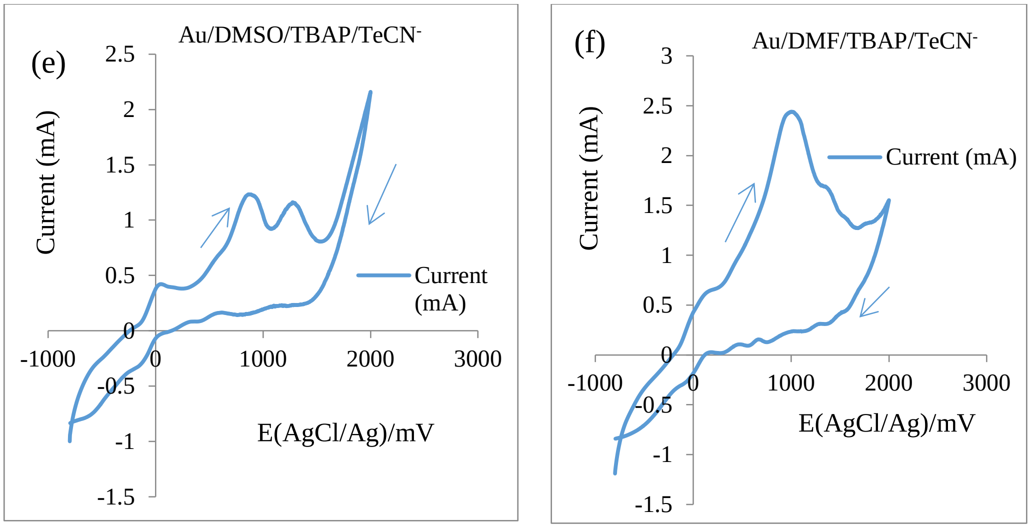


Figure 1: Cyclic voltammograms of the nickel, copper and gold electrodes in DMSO and DMF solvents containing tellurocyanate ions and 0.1 mol L^{-1} TBAP (sweep rate = 20 mV/s): (a) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (b) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF, (c) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (d) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF (e) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, and (f) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF. Arrows show the path actually traced upon conducting the sweep of potentials.

Figure 2(a) and (b) show the “single sweep voltammograms” which are effectively “slow-scan” voltammograms for the systems studied. These are the current-voltage plots for the systems obtained during the SNIFTIRS spectral acquisitions. In common with the CVs, there is a broad similarity in appearance for the single sweep voltammograms although the peaks observed occurr at different applied voltages between the different solvents. Differences in appearance between the CVs recorded under relatively faster scanning conditions and the single sweep voltammograms can be ascribed to mass transport issues in the thin layer. The plots in Fig 2(a) and (b) (and others) do not show the resistive tilt effect as the electrode has more time to respond to changes in the applied potential under the conditions of the SNIFTIRS experiment.

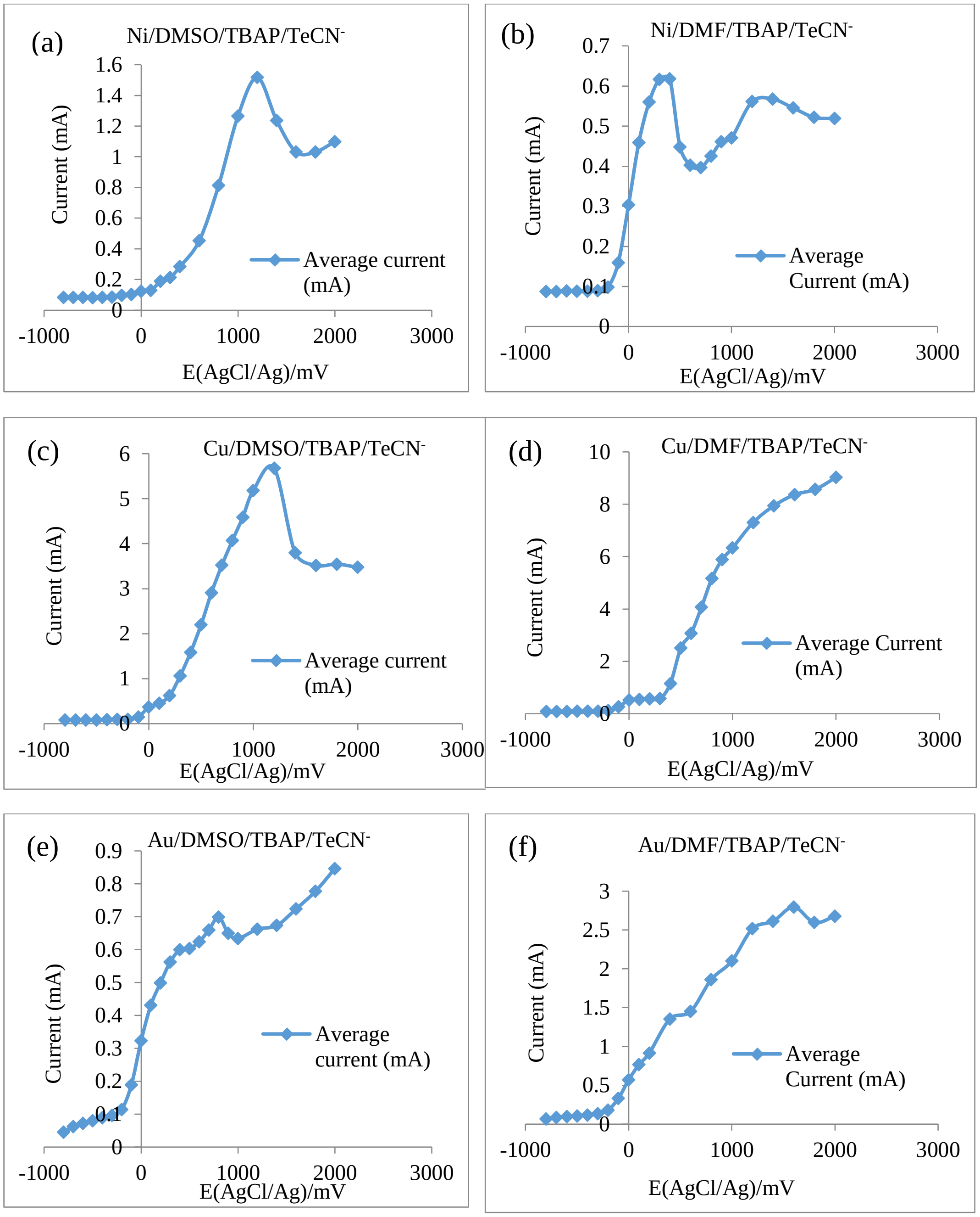


Figure 2: Single sweep voltammograms acquired of the nickel, copper and gold electrodes during a SNIFTIRS experiment in DMSO and DMF solvents containing tellurocyanate ions and 0.1 mol L^{-1} TBAP: Data were obtained from calculating the average current at the beginning and

end of the spectral acquisition period for each applied potential at which SNIFTIRS spectra were acquired. (a) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (b) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF, (c) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (d) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF (e) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO and (f) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF.

The suspicion of decomposition occurring in both systems studied was signalled by the observation that the Ni electrodes turned black when either the CV experiment was initiated or when a SNIFTIRS experiment was embarked upon. In later discussion on the SNIFTIRS spectra, more detail such as when the decomposition begins to occur on the electrode surface will be provided.

1.2 Cu/ $TeCN^-$/TBAP/DMSO and Cu/$TeCN^-$/TBAP/DMF electrochemical systems

Figure 1(c) and (d) show the cyclic voltammograms of the copper electrode in $TeCN^-$/TBAP/DMSO and $TeCN^-$/TBAP/DMF based electrolytes respectively. In contrast to the Ni electrode systems, there is a stronger similarity of appearance between the Cu electrode systems recorded in DMSO and in DMF. In addition, it is clear that the Cu electrode systems appear more reactive as the maximum anodic currents (8-10 mA) observed are 3-5 times the maximum currents observed in the Ni electrode systems (1.8-3 mA). Compared to the Ni electrode CVs, the Cu electrode systems are generally featureless and show merely an increase in current starting from negative currents at cathodic potentials to positive currents at anodic potentials. As stated earlier resistive tilt observed in some of the CVs would be caused by mass transport issues however the single sweep voltammograms do not exhibit this effect. In common with the Ni electrode systems, the Cu electrodes show evidence of decomposition of the $TeCN^-$ ion occurring in the electrochemical systems during CV and SNIFTIRS experiments.

1.3 Au/ $TeCN^-$/TBAP/DMSO and Au/$TeCN^-$/TBAP/DMF electrochemical systems

Figure 1(e) and (f) show the CVs of the gold electrode in $TeCN^-$/TBAP/DMSO and $TeCN^-$/TBAP/DMF based electrolytes respectively. The single sweep voltammograms are illustrated in Figure 2(e) and (f). In Figure 1(e) and (f), the Au electrode CVs only look similar in appearance below 0 mV (AgCl/Ag) but have different appearances in the anodic region above 0 mV (AgCl/Ag). In common with the other two electrode systems, a blackening of the electrode was observed suggesting decomposition of $TeCN^-$ ion had occurred at the electrode surface.

In conclusion, observations from the preliminary electrochemical investigations using cyclic voltammetry have shown evidence of the decomposition of the tellurocyanate ion during the electrical polarisation of the metal electrodes (Ni, Cu and Au). The cause of this decomposition is not due to water traces but due to the property of the tellurocyanate ion to destabilise when coming into contact with highly polarizing cations.[8, 9] This inherent chemical instability has precluded in the past[8] the isolation of such stable salts as potassium tellurocyanate for instance. In the case of the electrochemical systems being studied, the "ions" regarded as the fundamental cause for this decomposition are most likely the Ni^{2+}, Cu^+ and Au^+ ions which have formed during dissolution of the electrode during polarisation. SNIFTIRS and average current measurements have produced some insight into the point at which decomposition of the $TeCN^-$ ion occurred as well as the rate of decomposition, and the consequences on the speciation produced as a result of the decomposition in the three electrode systems studied.

2. *SNIFTIRS spectra of the Ni, Cu and Au electrodes in the presence of tellurocyanate ion.*

2.1. Ni/ $TeCN^-$/TBAP/DMSO and Ni/$TeCN^-$/TBAP/DMF electrochemical systems

Figure 3(a) and (b) represent SNIFTIRS spectra of the nickel electrode systems in DMSO and DMF respectively when electrically polarised in the presence of tellurocyanate ion. Table 1 summarises the FTIR data from the systems studied.

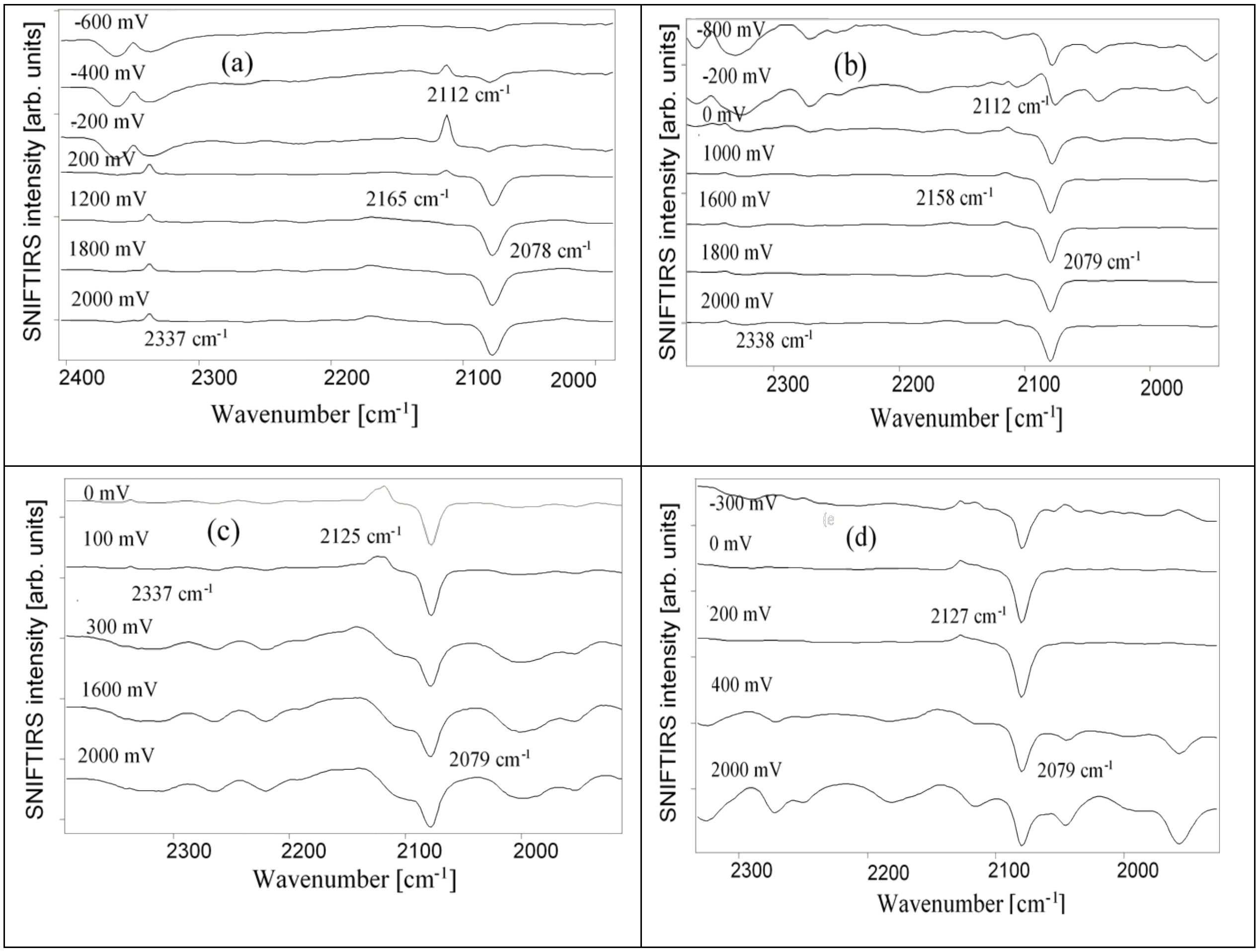
The most characteristic feature in the SNIFTIRS spectra of the Ni/$TeCN^-$/TBAP/DMSO and Ni/$TeCN^-$/TBAP/DMF systems is a negative-going peak at 2078-2079 cm^{-1} appearing at all potentials which can be clearly attributed to the ν(CN) stretching vibration of the $TeCN^-$ ion. This is always present as a *negative* going peak of varying intensity in spectra indicating it is present in greater amounts in the background spectrum, This negative feature becomes very noticeable spectrally at applied potentials > 0 mV(AgCl/Ag) where the decomposition of the $TeCN^-$ ion has proceeded rapidly

Table 1: FTIR data from in situ IR spectroelectrochemical studies of the Ni/$TeCN^-$, Cu/$TeCN^-$ and Au/$TeCN^-$ systems electrically polarized in 0.1 mol L^{-1} TBAP in DMSO or DMF solvents.

System studied	ν(CN) of free $TeCN^-$ ion cm^{-1}	ν(CN)[a] of Ni(II)/CN^- complex ion cm^{-1}	ν(CN)[a] of Cu(I)/CN^- complex ion cm^{-1}	ν(CN) of solid NCO^- (cyanate) species cm^{-1}	ν(CN)[a] of Au(I) /CN^- complex ion cm^{-1}	ν(CO) of CO_2 dissolved in solvent cm^{-1}	Colour of cell solution after SNIFTIRS experiment
Ni/DMF/$TeCN^-$	2078	2112		2158		2338	colourless
Cu /DMF/$TeCN^-$	2079		2127			2337	gold yellow
Au /DMF/$TeCN^-$	2079			2156		2337	colourless
Ni /DMSO/$TeCN^-$	2079	2112		2165		2337	colourless
Cu /DMSO/$TeCN^-$	2079		2125			2337	gold yellow
Au /DMSO/$TeCN^-$	2077				2140	nd	colourless

[a] Note that the $TeCN^-$ ion decomposed in the experiment so that ν(CN) stretching frequencies refer to complexes of the respective metal ions Ni(II), Cu(I) and Au(I) ions with CN^- ion rather than with $TeCN^-$. nd = not detected

As stated earlier, the observation of a negative going peak in all spectra indicates that there was more $TeCN^-$ ion in the original background spectrum acquired at -900 mV(AgCl/Ag) than at the potentials anodic to this background potential although the (negative) intensity of the peak does not increase in magnitude until the Ni electrode is adjusted to more positive potentials (see Figure 4(a) and (b). This and the observation of blackened electrodes (see earlier) in each system are proof that the tellurocyanate ion is decomposing in the thin layer cell when subjected to electrode polarisation especially in the regions where the nickel electrode is adjusted to potentials where Ni(II) ion species are obviously being produced.



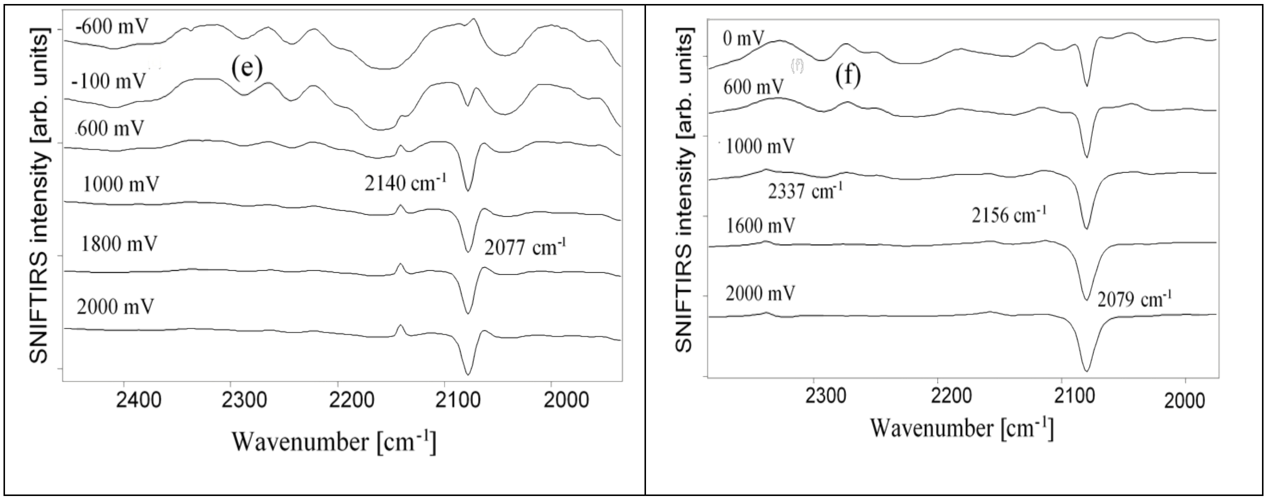
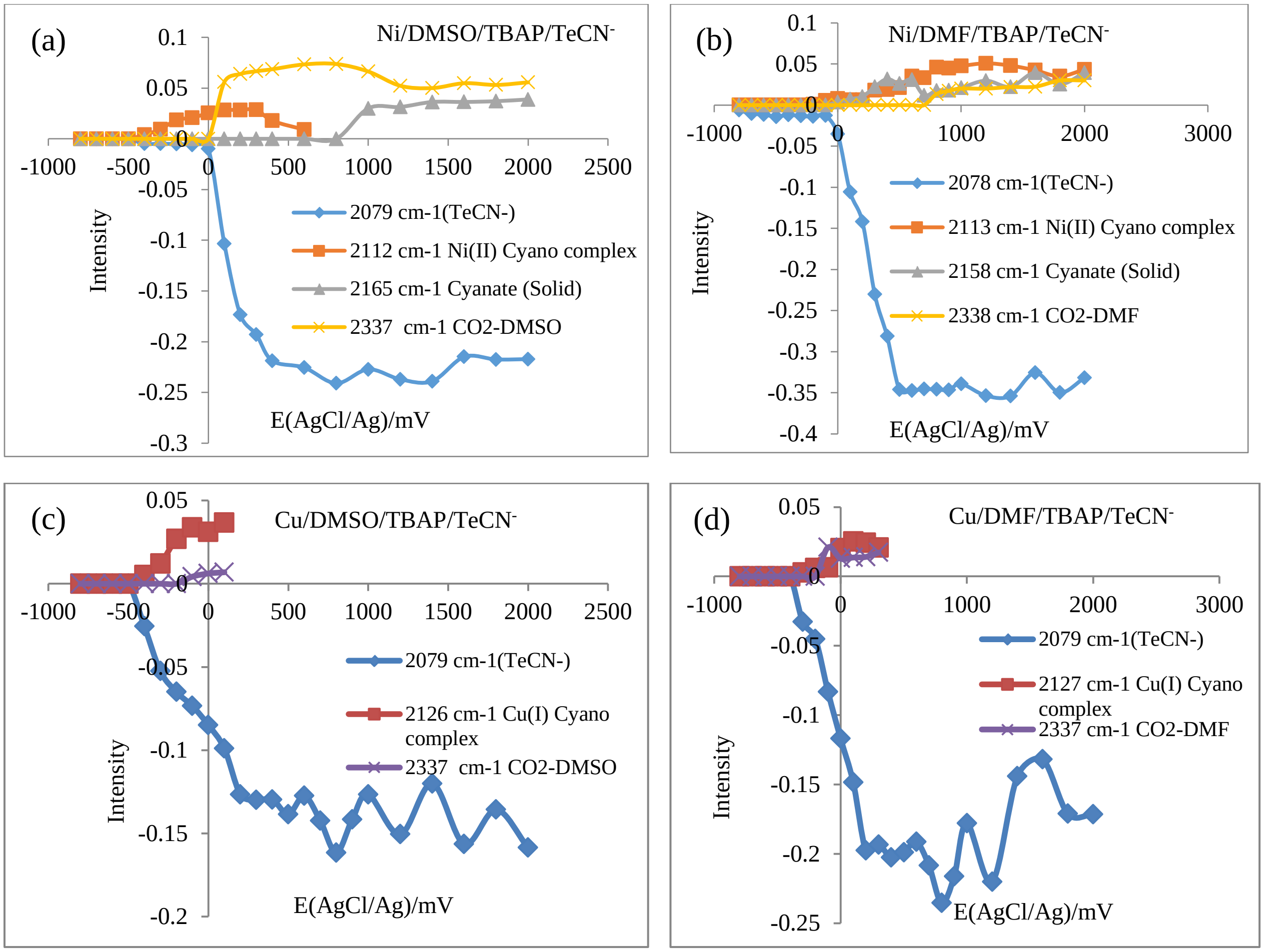


Figure 3: Series of SNIFTIRS spectra of the nickel, copper and gold electrodes as a function of applied potential in DMSO and DMF solvents containing tellurocyanate ions and 0.1 mol L^{-1} TBAP. (a) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (b) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF, (c) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (d) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF (e) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, and (f) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF.

The plots in Figure 4(a) and (b) as discussed constitute the electrochemical evidence that the $TeCN^-$ ion is decomposing and it was observed that the potential at which this began to occur on the Ni electrode surface was at -400 mV(AgCl/Ag)). At potentials more cathodic than this value, the intensity of the v(CN) stretching frequency peak of the $TeCN^-$ ion changes negligibly but after -400 mV (AgCl/Ag) it slowly becomes more negative and undergoes a very sharp decrease to even more greatly negative intensities after 0 mV(AgCl/Ag). The reason that the decomposition started to occur on the electrode is because at -400 mV (AgCl/Ag), a small amount of anodic dissolution (i.e. oxidation of Ni to Ni(II) ion) began to occur on the Ni electrode. Although the current increase in this region (i.e. between -400 mV(AgCl/Ag) is low initially, it increases significantly in the single sweep voltammograms see (Figure 2(a) and (b)) as the applied potential is adjusted to more anodic values The spectral evidence for Ni being oxidised to Ni(II) in the SNIFITRS spectra is provided by the fact that the intensity of the peak at

2112 cm^{-1} attributed to the species $[Ni(CN)_4]^{2-}$ (see later) also begins to increase in intensity from -400 mV(AgCl/Ag) and is maximised at +300 mV(AgCl.Ag). Hence, Ni^{2+} ions are being produced at the electrode which are causing the decomposition of the tellurocyanate ion, with the Ni^{2+} ions resultantly becoming complexed with the released CN^- ions. The $TeCN^-$ ion is hence sensitive to these ions when they are generated at the electrode surface.



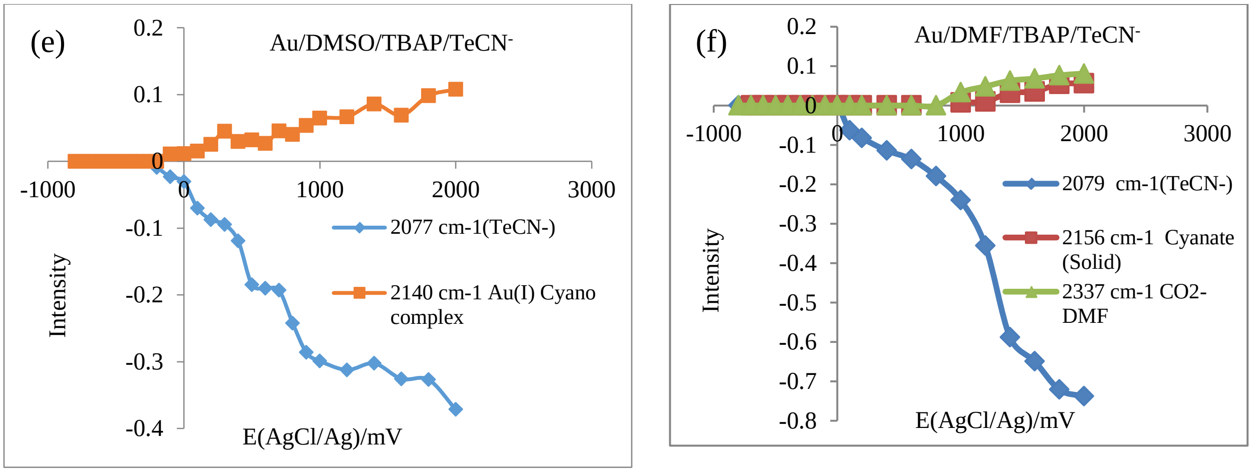


Figure 4: Plots of the intensity changes of the various molecular species generated in the thin layer during electrochemical polarisation and observed in the SNIFTIRS spectra as a function of applied potential in the nickel, copper and gold electrodes as a function of applied potential in DMSO and DMF solvents containing tellurocyanate ions and 0.1 mol L^{-1} TBAP. (a) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (b) Ni electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF, (c) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, (d) Cu electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF (e) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMSO, and (f) Au electrode and ~0.05 mol L^{-1} $TeCN^-$ in DMF.

In the SNIFTIRS spectra illustrated for both Ni/$TeCN^-$ systems studied (Figure 3(a) and (b)), other weak spectral features are evident. For example in the Ni/DMSO/$TeCN^-$ and Ni/DMF/$TeCN^-$ systems, a weak peak at 2112 cm^{-1} is observed. This peak as discussed earlier, can be confidently assigned to the ν(CN) stretching vibration of the species $[Ni(CN)_4]^{2-}$ in the *DMSO* or *DMF* solvent. Although the literature on the preparation of Ni-cyano complex ions in polar aprotic solvents is quite limited, a study by Semenishin[19] has reported an IR ν(CN) stretching frequency for $[Ni(CN)_4]^{2-}$ prepared in DMF and DMSO of 2117 cm^{-1} In the same study and others[20], it was also reported that there was a bathochromic shift of the IR stretching frequency when going from aqueous media to polar aprotic solvent media. In earlier reported Ni/CN^- SNIFTIRS studies[21] in *aqueous systems*, the corresponding ν(CN) stretching frequency for this species was reported to be 2124 cm^{-1} Hence the species at 2112 cm^{-1} in the present study can be assigned to $[Ni(CN)_4]^{2-}$ and not to species such as $[Ni(CN)_5]^{3-}$ which are known not to form in these polar aprotic solvents due to stronger bond formation of the metal ion with the DMSO or DMF solvent[19] The assignment of the 2112 cm^{-1} peak to $[Ni(CN)_4]^{2-}$ was also experimentally verified by model solution studies (in DMSO) where a solution of $[Ni(CN)_4]^{2-}$ was prepared independently via the addition of Ni^{2+} salts and KCN and also when Ni(II) salts were added to $TeCN^-$ ion directly) and its ν(CN) stretching frequency confirmed by transmission IR spectroscopy (see later). In terms of the SNIFTIRS experiment, the complex ion, $[Ni(CN)_4]^{2-}$ would have formed through the release of CN^- ion in solution from the decomposition of the $TeCN^-$ ion (see Scheme 1 for suggested half equation) and also because of the high thermodynamic stability of this ion (which in water, for instance, has a $\log(\beta_4 /(\text{mol L}^{-1})^4$value of 30.5 ± 0.3.[22])

$$4TeCN^- + Ni_{(s)} \rightarrow [Ni(CN)_4]^{2-} + 4Te_{(s)} + 2e^- \qquad \text{(Scheme 1)}$$

The species though stable, does not constitute a very dominant feature in the SNIFTIRS spectra. It is suspected that the electrode surface has become modified by the Te layer deposited such that only a small amount of the Ni/cyanide complex can form due to a blocking effect.

Other peaks observed in Figure 3(a) and (b) were weak and broad features from 2158-2165 cm^{-1} It is believed that these are due to the ν(CN) stretching frequencies of solid cyanate species, i.e. KOCN(s) that have formed on the electrode during the in situ IR experiment. These will have formed as a result of CN^- ion oxidation at the electrode surface. The source of the CN^- ion may be from the $[Ni(CN)_4]^{2-}$ complex, especially in the Ni/$TeCN^-$/TBAP/DMSO electrochemical system where the spectral intensity of the peak assigned to $[Ni(CN)_4]^{2-}$ is observed to decrease to zero when the peak due to KOCN(s) starts to appear in spectra (see Figure 4(a)). The reason for observing KOCN(s) in the Ni/TeCN$^-$ system is due to the low solubility of the NCO$^-$ ion in DMSO, which would be exacerbated by the fact that thin layer conditions were being used that are prone to supersaturation if a low solubility species (in the solvent being used) was being electrogenerated. Earlier SNIFTIRS studies involving cyanate ion in DMSO or DMF have used concentrations of half the value of 0.05 mol L^{-1} (the expected value of [CN$^-$] if generated from the decomposition of 0.05 mol L^{-1} TeCN$^-$ ion assuming a 1:1 stoichiometry) ions) at which cyanate ion is known to be soluble from experimental experience. Hence, the reason for only seeing a peak attributable to solid KOCN (as opposed to a solution species) is due to the fact that it is being produced in the thin layer at a concentration that exceeds its solubility in DMSO. Had soluble cyanate species been detected, a peak at the lower wavenumber value of 2137 cm^{-1} as has been observed in previous SNIFTIRS studies in this solvent, would have been detected[5]

In the Ni/TeCN$^-$/TBAP/DMF electrochemical system, the spectral intensity trend for the $[Ni(CN)_4]^{2-}$ ion is not so clear-cut but does show a reduction in intensity at very anodic potentials where the KOCN(s) formation is observed to occur. An additional feature observed in SNIFTIRS spectra is the appearance of a weak peak at 2337-2338 cm^{-1} which can be assigned on the basis of earlier studies[5] to dissolved CO_2 in the DMSO or DMF solvent. This peak was at its most intense only in the Ni/DMSO/TeCN$^-$ system (Cu and Au electrode systems either showed minor CO_2 content or none). In contrast, CO_2-associated peaks were weak or non-existent in the DMF solvent-based system of Ni. This CO_2 is electrogenerated during the in situ IR studies and has arisen from oxidation of either the DMSO solvent or, more likely from the liberated cyanide via decomposition of TeCN$^-$ at the electrode.

2.2. Cu/ TeCN$^-$/TBAP/DMSO and Cu/TeCN$^-$/TBAP/DMF electrochemical systems

Figure 3(c) and (d) illustrate the in situ IR (SNIFTIRS) spectra for the Cu/TeCN$^-$/TBAP/DMSO or DMF electrochemical systems. Figure 4(c) and (d) are graphs showing the intensity trends of species detected in the in situ IR experiments. Table 1 summarises the IR data from this system. As observed in the Ni electrode systems studied, the (negative-going) peak due to the TeCN$^-$ ion at 2079 cm^{-1} was an important feature in the spectrum with the negative intensity indicating decomposition over part of the range of the applied potentials studied. The spectral intensity graphs of detected species as a function of applied potential (Figure 4(c) and (d)) confirm that the decomposition of the TeCN$^-$ ion is accelerated as the electrode is increasingly polarized in the anodic direction of potential with a starting point of approximately -500 mV (AgCl/Ag). On Ni , the decomposition of TeCN$^-$ ion starts to occur at approximately

-400 mV(AgCl/Ag). The earlier decomposition (though small) of the TeCN$^-$ ion on the Cu electrode (starting at -500 mV(AgCl/Ag)) is due to the greater reactivity of the Cu electrode when it is immersed in the DMSO or DMF solvent and would indicate that Cu(I) species are being released from the electrode at these more cathodic applied potentials relative to Ni. As in the Ni electrode case, these released Cu(I) ions are likely to be destabilising the TeCN$^-$ ion so leading to its decomposition into Te and CN$^-$

At the same potential that the decomposition of TeCN$^-$ ion is observed to occur on the Cu electrode (from -500 mV(AgCl/Ag)), weak, broad peaks at 2125-2127 cm^{-1} are observed to occur in the SNIFTIRS spectra of the Cu/DMSO/TeCN$^-$ and Cu/DMF/TeCN$^-$ systems (see Figure 3(c) and (d). These are presumed on the basis of earlier in situ IR studies of Cu/CN$^-$ systems[23] to be due to the $[Cu(CN)_2]^-$ ion. As these are forming at the time the TeCN$^-$ ion is beginning to decompose, we propose that these electrogenerated Cu$^+$ ions are causing the decomposition and reacting with the released CN^- ions with a suggested formation half equation shown in Scheme 2 of:

$$2TeCN^- + Cu_{(s)} \rightarrow [Cu(CN)_2]^- + 2Te + e^- \quad \text{(Scheme 2)}$$

In support of this, model solution IR data from solutions prepared from mixing Cu(II) salts and CN^- ion in DMSO have convincingly shown that this peak is in fact due to the Cu(I) species, $[Cu(CN)_2]^-$ (see later).

Additional features observed in the spectral intensity vs applied potential plots (Figure 4(c) and (d)) that also suggest the inherently greater reactivity of the Cu electrode systems are fluctuations in the observed intensity trends visible only at very high anodic applied potentials. This behaviour might be associated with reactive electrochemical systems showing a degree of turbulence or disturbance in the thin layer due to chemical changes caused through application of the very positive potentials to the electrode surface. This would affect intensities of species referenced to a background potential where activity in the thin layer is relatively more quiescent.

2.3. Au/ $TeCN^-$/TBAP/DMSO and Au/$TeCN^-$/TBAP/DMF electrochemical systems

Figure 3(e) and (f) illustrate the SNIFTIRS spectra for the Au/$TeCN^-$/TBAP/DMSO or DMF electrochemical systems. Figure 4(e) and (f) are graphs showing the intensity trends of species detected in the SNIFTIRS experiments. Table 1 summarises the IR data from this system. As observed in the Cu and Ni electrode systems studied, the (negative-going) peak due to the $TeCN^-$ ion at 2079 cm^{-1} was an important feature in the spectrum with the negative intensity also suggesting that the $TeCN^-$ ion is decomposing on the Au electrode systems over the range of the applied potentials studied. The spectral intensity graphs of detected species as a function of applied potential (Figure 4(e) and (f)) confirm that the decomposition of the $TeCN^-$ ion accelerates as the electrode is increasingly polarized in the anodic direction of potential. On Au, however, the potential at which this decomposition begins to occur is approximately -200 mV (AgCl/Ag).This event is paralleled in the Au/DMSO/$TeCN^-$ SNIFTIRS spectra by an increase in intensity of a peak at 2140 cm^{-1} (see Figure 4(e) and (f)) which has been assigned to the ν(CN) stretching frequency of the complex ion, $[Au(CN)_2]^-$ (see later). This indicates that the Au electrode is beginning to dissolve to form Au^+ ions around this potential which is in turn destabilising the $TeCN^-$ ion. Compared to the Ni and Cu system intensity data for this species, the *rate of decline* of the $TeCN^-$ species on the Au electrode as indicated by the intensity curve for the peak at 2079 cm^{-1} as a function of applied potential , is less acute. This suggests that on Au, decomposition is not as active which agrees with the fact that Au^+ as a cation has lower polarising power relative to Cu^+ and Ni^{2+} ions.

In the Au/DMF/$TeCN^-$ SNIFTIRS spectrum, even though there is no characteristic peak due to $[Au(CN)_2]^-$ but weak peaks due to solid KOCN (2156 cm^{-1}) and CO_2 (2337 cm^{-1}) [5, 6], it is still obvious from the intensity/potential plots that $TeCN^-$ decomposes in this system. It is thus posited that Au is still dissolving in some form in this system to form Au^+ (which in turn is causing the decomposition of the $TeCN^-$ ion) even though the presence of Au^+ is not able to be verified in SNIFTIRS spectra. The reason for there being no observation of $[Au(CN)_2]^-$ in the DMF-based system is most likely due to the lower solubility of KOCN (an oxidation product of CN^-) in the DMF solvent used. Indeed, this lack of solubility of KOCN in DMF was confirmed when making different model solutions of various metal salt:potassium cyanate mole ratios in DMF and DMSO (see later).

As mentioned earlier, SNIFTIRS spectra for the Au/DMSO/$TeCN^-$ system (Figure 4(e)), featured a weak peak at 2140 cm^{-1} which can be assigned to the $[Au(CN)_2]^-$ ion.[6, 24] In DMSO this would have formed from an interaction between the electrogenerated Au(I) ion with the tellurocyanate ion so causing its decomposition with release of cyanide ion that would have subsequently complexed the Au^+ ion to form $[Au(CN)_2]^-$. (see Scheme 3 for suggested half equation demonstrating its formation)

$$2TeCN^- + Au_{(s)} \rightarrow [Au(CN)_2]^- + 2Te + e^- \quad \text{(Scheme 3)}$$

The formation of this ion is not surprising as the $[Au(CN)_2]^-$ complex ion has one of the highest thermodynamic stabilities known.[25] Its formation would be far more highly favoured over a complex ion of Au(I) with $TeCN^-$ ion for instance, the formation of which would be precluded anyway by the mild polarising power of Au(I) ions.

3. *IR data from the model solutions prepared from mixing Ni(II) and Cu(II) salts with tellurocyanate solutions prepared in DMSO*

Model solutions were prepared to verify the assignments made for peaks observed in the Ni and Cu SNIFTIRS spectra as discussed above. Gold/tellurocyanate model solutions were not generated in this study. The model solution methodology has been used in earlier studies for confirming[5] electrochemically generated species via an electrochemically independent generation method. These solutions were prepared by direct addition of solid Ni(II) and Cu(II) salts to freshly generated solutions of $TeCN^-$ ion in DMSO. Figure 5 illustrates the model solution spectra for Ni(II) and Cu(II) ions interacting with the tellurocyanate solution generated in DMSO. Figure 5(a) is the IR spectrum of the free tellurocyanate ion when it is prepared from the reaction of elemental tellurium with potassium cyanide. The intense peak at *ca.* 2078 cm^{-1} is due to the ν(CN) stretching frequency of the $TeCN^-$ ion.[9] Figure 5(b) and 5(c) represent the spectra obtained from mixtures of $TeCN^-$ ion with Cu(II) and Ni(II) salts respectively in the mole ratio, metal ion (Cu(II) or Ni(II)) : $TeCN^-$ ion of 1:2 .

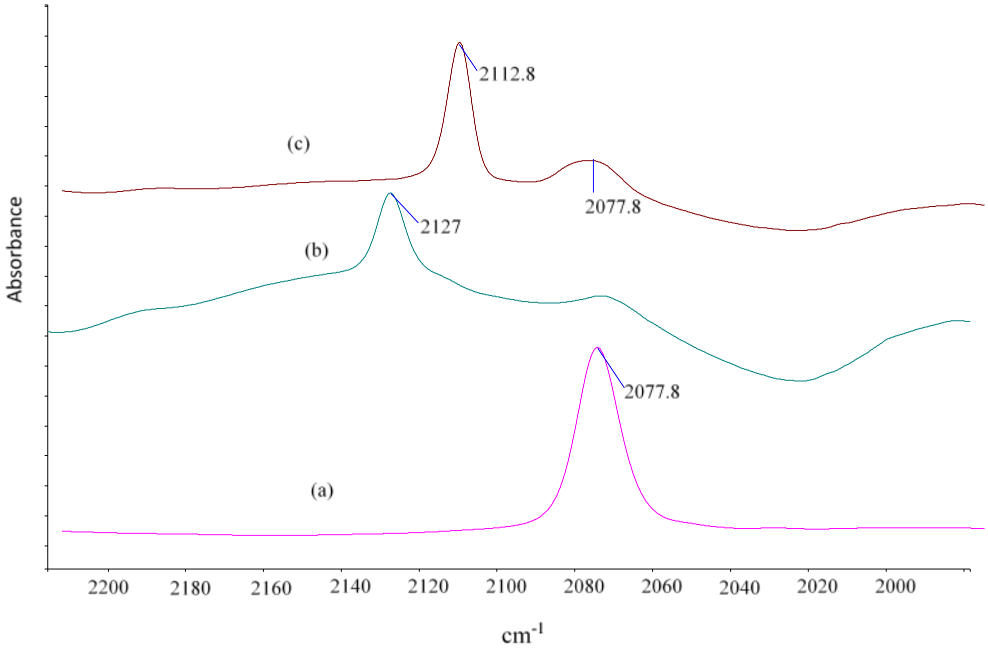


Figure 5: IR transmission spectra for (a) the pale yellow solution of tellurocyanate ion generated in DMSO from reaction of the 1:1 mole ratio mixture of finely ground elemental Te and KCN, (b) 1:2 mole ratio model solution prepared from mixing partially dehydrated $CuCl_2$ (0.025 mol L^{-1}) and $TeCN^-$ (~0.05 mol L^{-1}) in DMSO (solution observed to deposit black solid), and (c) 1:2 mole ratio model solution prepared from mixing partially dehydrated $Ni(NO_3)_2$ (0.025 mol L^{-1}) and $TeCN^-$ (~0.05 mol L^{-1}) in DMSO (solution observed to deposit black solid).

However, when adding Ni(II) or Cu(II) metal salts to solutions of free $TeCN^-$ ion in DMSO, an immediate reaction was observed to occur which resulted in the formation of a black solid that deposited in the reaction container. This was a firm indication that the $TeCN^-$ ion was very unstable in the presence of Ni(II) and Cu(II) ions with decomposition of the ion into black finely divided elemental Te and free cyanide ion [9] being a likely consequence. This result is not only expected given the work of Austad et al.[9] in proving that the $TeCN^-$ ion is unstable in the presence of highly polarizing cations but also strengthens the above interpretations of the SNIFTIRS spectra regarding the instability of the $TeCN^-$ ion when metal ions begin to be released from polarisation-induced dissolution of the electrodes in the studied systems. This property of the $TeCN^-$ ion may be of utility as a highly sensitive and reactive "marker" to the presence or release of oxidised, soluble metal species on electrodes. Although the $TeCN^-$ ion has decomposed in the model solutions, the IR spectra of these solutions (Figure 5(b) and 5(c)) clearly feature two weak peaks at 2127 cm^{-1} and 2112.8 cm^{-1} respectively for the Cu(II)/$TeCN^-$ and Ni(II)/$TeCN^-$ model solutions. These can be assigned with reasonable confidence on the basis of similar observations (for the Cu/CN^- system from earlier work[23]) to the $[Cu(CN)_2]^-$ ion (*ca.* 2127 cm^{-1}) and the $[Ni(CN)_4]^{2-}$ ion (*ca.* 2112 cm^{-1})[19]. These assignments were further experimentally proven by recording FTIR transmission spectra of other model solutions prepared by mixing Ni(II) and Cu(II) salts with KCN salt in DMSO in various Ni(II):KCN and Cu(II):KCN mole ratios varying from 1:1 to 1:4 (see Table 2 for FTIR data). In all the Ni/KCN model solutions examined by transmission FTIR, a single peak at *ca.* 2112 cm^{-1} was observed which can be assigned to the $[Ni(CN)_4]^{2-}$ complex ion in this solvent. This hence proves the identity of the peak observed at this value in the SNIFTIRS spectra discussed earlier for Ni electrodes electrically polarized in the presence of $TeCN^-$ ion in DMF and DMSO-based electrolytes.

Table 2: FTIR data from IR studies of DMSO model solutions of $Ni(NO_3)_2$ and $CuCl_2$ and potassium cyanide salts prepared with different mole ratios.

Model solution studied and mole ratio of $Ni(NO_3)_2$ or ($CuCl_2$): KCNprepared in DMSO	ν(CN) of free NCO^- ion or cyanate-containing complex ion species cm^{-1}	ν(CN) of Ni(II) and Cu(I)/CN^- complex ion species cm^{-1}	ν(CO) of CO_2 dissolved in solvent cm^{-1}	Observed colour of model solution preparations
DMSO				
$Ni(NO_3)_2$/ KCN 1:1		2112[a]	nd	colourless
$Ni(NO_3)_2$/ KCN 1:2		2112	nd	colourless
$Ni(NO_3)_2$/ KCN 1:4		2112	nd	colourless
$CuCl_2$/ KCN 1:1	2224[b] (s), 2200[c] (sh)	2127[d]	2337	gold yellow
$CuCl_2$/ KCN 1:2	2224 (s)	2127	2337	gold yellow

nd = not detected, s= strong, sh=shoulder

[a] $[Ni(CN)_4]^{2-}$ [19] [b] $[Cu(NCO)_2]^-$ [26], [c] $[Cu(NCO)_4]^{2-}$ [27], [d]$[Cu(CN)_2]^-$ [28]

In the case of the model solutions prepared by mixing $TeCN^-$ or CN^- with Cu(II) salts, some fortuitous redox chemistry has occurred between (effectively) CN^- ion and Cu(II) ions to produce the $[Cu(I)(CN)_2]^-$ species observed (which also featured in the Cu/$TeCN^-$ SNIFTIRS spectra)

In Figure 5(b), the peak at 2127 cm^{-1} arose from the destabilisation of $TeCN^-$ caused by the presence of the polarising Cu^{2+} ions (from the Cu(II) salt) which led to the release of free CN^- ion. This then reacted with Cu(II) ions in a fortuitous redox side-reaction[29] (known to occur between Cu(II) and pseudohalide ions) so leading to Cu(I) species being present in the mixture which then became complexed with CN^- ion to form the $[Cu(CN)_2]^-$ species that gives rise to the peak at 2127 cm^{-1}.

In the IR spectra (See Figure 6) of model solutions prepared from mixing Cu(II) salts with KCN salt in different $CuCl_2$:KCN mole ratios in DMSO, the fortuitous redox chemistry was also observed which led to the appearance of the 2127 cm^{-1} peak due to $[Cu(CN)_2]^-$ as well as additional peaks at 2224 cm^{-1} (shoulder at 2200 cm^{-1}) and at 2337 cm^{-1}. These have been assigned to $[Cu(I)(NCO)_2]^-$ [26], $[Cu(II)(NCO)_4]^{2-}$ [27] and CO_2 dissolved in the DMSO solvent [5]. These species are all obviously due to the products of the redox reaction. The shoulder peak at 2200 cm^{-1} due ostensibly to Cu(II)-isocyanato complex ion species disappeared when more cyanide ion was supplied in the solution. This served to reduce more Cu(II) to Cu(I). These species were not relevant to the SNIFTIRS spectra but merely observed as side products in the transmission IR spectra of these Cu-based model solutions.

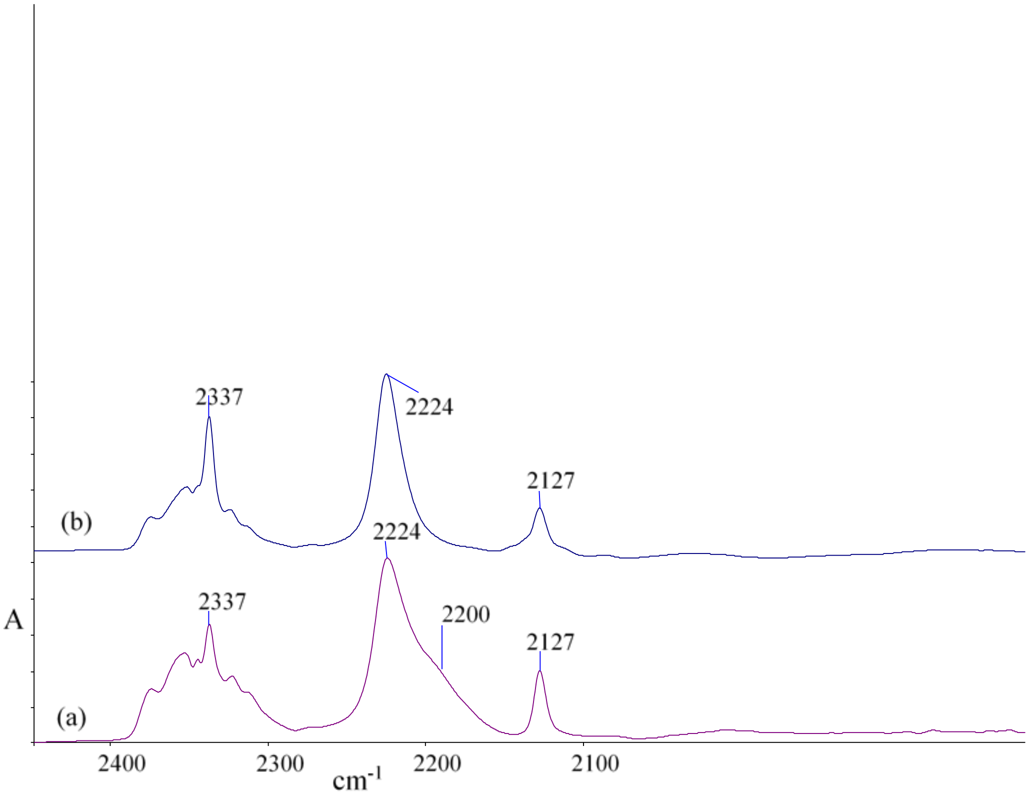


Figure 6: IR transmission spectra for (a) the 1:1 mole ratio model solution for $CuCl_2$: KCN in DMSO prepared from mixing partially dehydrated $CuCl_2$ (0.025 mol L^{-1}) and KCN (0.025 mol L^{-1}) in DMSO (solution), (b) 1:2 mole ratio model solution for $CuCl_2$: KCN in DMSO.

CONCLUSION

In general, IR spectroelectrochemical studies of the anodic dissolution of Ni, Cu and Au in DMSO and DMF solutions of the unstable $TeCN^-$ ion have been presented for the first time and have conclusively shown via the observation of by-products formed at the electrode that the $TeCN^-$ ion decomposes in polarized electrochemical cells at certain potentials to form CN^- ion and a black substance which would be elemental tellurium. The cause of the decomposition is due to the generation of dissolved metal ions from the electrode which destabilise the $TeCN^-$ ion due to their polarising power with the destabilising effect increasing in the order $Au^+ > Cu^+ > Ni^{2+}$. This agrees with the known trends with regard to polarising power for these cations [30]. The CN^- ion from the decomposition then goes on in these systems to become incorporated in metal complex ions generated from the electrochemically induced dissolution of the metal electrodes. This was shown through comparison of observed IR data from SNIFTIRS experiments with transmission IR data of model solution experiments (in DMSO) where Ni(II) and Cu(II) salts were codissolved in solution with $TeCN^-$ and CN^-. In general the tendency of the $TeCN^-$ ion to decompose in electrochemically polarized systems where metal ions are being formed is reflective of its well-known, chemical instability in the presence of highly polarizing cations. The effect may be of use for developing sensors to detect when soluble ions from electrodissolved metals are generated at electrodes.

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REFERENCES

1. E. Herrero, A. Rodes, J. M. Pérez, J. M. Feliu and A. Aldaz, *Journal of Electroanalytical Chemistry*, 1996, **412**, 165-174.
2. E. Herrero, M. J. Llorca, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, 1995, **383**, 145-154.
3. E. Herrero, M. J. Llorca, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, 1995, **394**, 161-167.
4. S. Ham, B. Choi, N. Myung, N. R. de Tacconi, C. R. Chenthamarakshan, K. Rajeshwar and Y. Son, *Journal of Electroanalytical Chemistry*, 2007, **601**, 77-82.
5. L. K. H. K. Alwis, M. R. Mucalo and B. Ingham, *J. Electrochem. Soc.*, 2013, **160**, H803-H812.
6. L. K. H. K. Alwis and M. Mucalo, *J. Electrochem. Soc.*, 2014, **161**, H738-H750.
7. K. H. K. L. Alwis, B. Ingham, M. R. Mucalo, P. Kappen and C. Glover, *RSC Advances*, 2015, **5**, 15709-15718.
8. A. W. Downs, *Chemical Communications*, 1968, 1290-1291.
9. T. Austad and J. Songstad, *Acta. Chem. Scand.*, 1971, **25**, 331-333.
10. O. H. Ellestad, P. Klaeboe and J. Songstad, *Acta Chem. Scand.*,, 1972, **26**, 1724-1726.
11. H. K. Spencer, M. V. Lakshmikantham and M. P. Cava, *Journal of the American Chemical Society*, 1977, **99**, 1470-1473.
12. A. Z. Al-Rubaie, in *New Developments in Organometallic Chemistry Research*, ed. M. A. Cato, Nova Science, New York, 2004, pp. 191-213.
13. P. Klaeboe, C. J. Nielsen and J. Songstad, *Acta Chem. Scand. A*, 1977, **31**, 884-886.
14. G. Cauquis and G. Pierre, *Bull. Soc. Chim. Fr.*, 1976, 736-738.
15. C. Korzeniewski, in *Handbook of Vibrational Spectroscopy*, eds. J. M. Chalmers and P. R. Griffiths, John Wiley, New York, 2002, p. 2700.
16. W. M. Keely and H. W. Maynor, *J. Chem. Eng. Data*, 1963, **8**, 297-300.
17. J. Wang, J. Harris, M. Li, D. Plana, M. E. Barbour, D. J. Fermin and S. Mann, *CrystEngComm*, 2013, **15**, 7152-7156.
18. A. Heather, in *Nanostructured Ceramic Oxides for Supercapacitor Applications*, CRC Press, 2014, pp. 71-118.
19. D. I. Semenishin, *Ukr. Khim. Zh. (Russ. Ed.)*, 1998, **64**, 85-87.
20. N. M. Levinson, S. D. Fried and S. G. Boxer, *The Journal of Physical Chemistry B*, 2012, **116**, 10470-10476.
21. M. R. Mucalo, R. P. Cooney and G. A. Wright, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 1083-1086.
22. W. Beck, *Pure & App. Chem*, 1987, **59**, 1703-1720.
23. K. A. B. Lee, K. Kunimatsu, J. G. Gordon, W. G. Golden and H. Seki, *J. Elec. Soc.*, 1987, **134**, 1376-1678.
24. K. Kunimatsu, H. Seki, W. G. Golden, J. G. Gordon and M. R. Philpott, *Langmuir*, 1988, **4**, 337-341.
25. J. Emsley, *The Elements*, Second edn., Clarendon press- Oxford, 1991.
26. A. Ray, G. M. Rosair, R. Rajeev, R. B. Sunoj, E. Rentschler and S. Mitra, *Dalton Trans.*, 2009, 9510-9519.
27. J. L. Burmeister and T. P. O'Sullivan, *Inorganica Chemica Acta*, 1969, **3**, 479-486.

28. K. A. B. Lee, K. Kunimatsu, J. G. Gordon, W. G. Golden and H. Seki, *J. Electrochem. Soc.*, 1987, **134**, 1676-1678.
29. S. K. Tobia, E. R. Souaya and W. G. Hanna, *Polyhedron*, 1985, **4**, 425-428.
30. S. Prakash, *Modern Inorganic Chemistry*, S Chand & Co. Ltd, India, May, 1987.