ANODIC OXIDATION OF CYANIDE AND CYANATE IONS ON A PLATINUM ELECTRODE

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Received 12 December 1986; in final form 27 January 1987

The oxidation processes of cyanide and cyanate ions on a Pt electrode in aqueous and methanol solutions were studied by infrared spectroscopy. In aqueous solution, the cyanide ion was oxidized to cyanate and successively to carbon dioxide. The reaction proceeded on an oxidized platinum surface. In methanol solution, HNCO is the main product during anodization.

1. Introduction

The development of infrared reflection-absorption spectroscopy (IRRAS) has provided molecular vibrational information on adsorbed species on an electrode surface. The spectral intensities as well as the frequencies of the adsorbate vibrational modes are perturbed from those for the bulk species in the solution. These pieces of information, combined with the surface selection rule, can reveal the vibrational modes of surface bonding, adsorbate orientation and the reaction mechanisms of the adsorbates on the electrode surfaces under applied potentials.

As already published [1], the cyanide ion (CN⁻) is oxidized to cyanate (OCN⁻) on a platinum electrode. In the present report we describe the further oxidation of OCN- to carbon dioxide and the reaction mechanisms on the electrode during the anodization of CN⁻. The adsorption of CN⁻ and OCN⁻ on Ag [2] and Au [3] electrodes has recently been reported in relation to surface-enhanced Raman spectroscopy (SERS). However, a greater variety of electrode reactions are expected on the platinum surface. The oxidation of adsorbed CO on Pt to carbon dioxide has been investigated extensively by electrochemical [4] and spectroscopical techniques [5]. The rate-determining step is the reaction of adsorbed CO with adsorbed atomic oxygen. Both CN⁻ and OCN⁻ are also expected to react with an adsorbed oxygen atom on the platinum surface. These ions are not oxidized in an non-aqueous solution, and different reactions occur in methanol solution.

2. Experimental

The details of the polarization modulation IRRAS (PM IRRAS) spectrometer and the electrochemical cell have been described elsewhere [1,6]. The IRRAS spectrometer used was a Perkin–Elmer 983G infrared spectrometer combined with a reflection attachment. The pretreatment of the working electrode was the same as that in ref. [1]. The reference electrode was Ag/AgCl (saturated KCl). Reagent grade KCN, KOCN, KCl and anhydrous LiCl were used without further purification. Spectrograde CH₃OH was purified by distillation. The potential–reflectivity curve was measured at a fixed wavelength (2.5 μ m) where no absorption band exists. The potential sweep was started at -0.5 V toward the anodic direction at a rate of 5 mV/s.

It is important to note that the interpretation of the PM IRRAS and IRRAS spectra differ from each other. In the thin-layer electrochemical cell geometry, the incident infrared beam passes through the bevelled edge of a CaF₂ window into a thin solution layer and is reflected at the Pt electrode surface. The thickness of the solution layer between the CaF₂ window and the electrode reaches several micrometers. Therefore in an IRRAS experiment, which measures the relative changes in the reflected infrared intensities, $\Delta R/R_0$, the spectra show not only the adsorbed species on a Pt electrode but also all the solution species that are present between the window and the electrode. Since the absorption intensity due to the adsorbed species is much smaller than that of the

0 009-2614/87/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) solution species, the method is suitable for the detection of solution species, such as reactants or products in the course of the electrode reactions. In PM IRRAS experiment, on the other hand, the absorption of bulk-phase solution species is mostly cancelled by the phase-sensitive detection of I_p and I_s signals, and surface species are detected with enhancement. Therefore, the PM IRRAS method is sensitive to surface species.

3. Results and discussion

3.1. Oxidation in aqueous solution

Fig. 1 shows the IRRAS spectra obtained for 0.1 mol/l KCN and 0.1 mol/l KCl aqueous solution. The



Fig. 1. Change in the IRRAS spectrum for $0.1 \mod \ell R$ KCN in 0.1 mol/ ℓ KCl aqueous solution as a function of the electrode potential.

spectra were plotted by subtracting the spectrum from the reference ones measured at -0.5 V where no oxidation reaction occurs. At more negative potentials no detectable IRRAS bands were obtained in the frequency region 2400-2000 cm⁻¹. An intense absorption band starts to appear in 2170 cm^{-1} above 0.4 V. This band can be assigned to the antisymmetric vibration of OCN- formed by oxidation of CN^{-} [1]. The intensity of this band reaches its maximum at 0.6 V and gradually decreases at more positive potentials. On the other hand, a sharp band at 2342 cm⁻¹ and a weak band at 2260 cm⁻¹ start to appear at 0.6 V and increase in intensity with a further anodic potential sweep. The fact that the two bands appear after the appearance of the 2170 cm^{-1} band (OCN⁻) and develop in accordance with the decrease of the 2170 cm^{-1} band indicates that the electrogenerated OCN- species undergoes a further oxidation reaction to give CO₂ and a species which gives rise to the band at 2260 cm⁻¹. In order to confirm this conjecture, we examined the IRRAS measurement in a aqueous KOCN solution. As expected in this case, an intense band at 2342 cm^{-1} and a weak band at 2260 cm^{-1} can be observed in the anodic potential region at the expense of the intensity of the OCN^{-} band. The band at 2342 cm⁻¹ is definitely assigned to CO₂ because of its frequency. The evolution of CO_2 implies that the dissociation of the OCN molecule occurs at the electrode surface. The residual nitrogen atom would combine with another nitrogen atom on the electrode surface to form a nitrogen molecule [7],

$$NCO_{ad} + O_{ad} \rightarrow CO_2 + N_2 . \tag{1}$$

Furthermore, formation of isocyanic acid (HNCO) can be expected in the anodic potential region,

$$NCO_{ad} + H_{ad} \rightarrow HNCO$$
. (2)

The N-C stretching vibration of HNCO has been observed between 2260 and 2274 cm⁻¹ [8,9]. Thus we assign the 2260 cm⁻¹ band seen above 0.6 V to HNCO. Another piece of evidence for the assignment comes from the IRRAS measurements in nonaqueous solvents, as described below.

In order to clarify the detailed mechanism of the above oxidation reactions at the electrode surface, we investigated the potential dependence of the adsorbed CN^- on a Pt electrode by PM IRRAS. The adsorbed



Fig. 2. (a) Potential dependence of the integrated intensity of adsorbed cyanides. (b) Reflectivity-potential curves of Pt electrode in the absence (upper) and in the presence (lower) of 0.01 mol/ ℓ KCN in 0.1 mol/ ℓ KCl aqueous solution.

 CN^- exhibited an absorption band at 2090–2130 cm^{-1} in the PM IRRAS spectra [5,6]. The 5 σ electron donation due to CN^- coordination strengthens the C-N bond because the highest occupied 5 σ orbital is a bonding orbital between the metal and the adsorbate CN^- , but an antibonding one with respect to the C-N bond [10][‡]. Fig. 2a shows the change in the integrated absorption intensity of the adsorbed CN^- as a function of the electrode potentials. Initially the coverage decreases gradually with the anodic potential sweep and rapidly reduces to zero above 0.4 V.

The desorption of CN^- in the anodic potential region can be explained by the formation of a platinum oxide layer.

The formation of a surface oxide layer is easily detectable by a reflection measurement. The ratio $\Delta R/R_0$ decreases markedly when the surface oxide layer starts to grow because of its large absorption coefficients [11], thus the degree of surface oxidation can be estimated from the amount of decrease in $\Delta R/R_0$. Fig. 2b shows the potential dependence of the reflectivity. When the solution contains no CN-(upper curve), the reflectivity starts to decrease at about -0.3 V. Thus the formation of a surface oxide layer starts at -0.3 V. In the presence of 0.01 mol/ ℓ KCN (lower curve), however, the reflectivity decreases very slowly up to 0.4 V and reduces rapidly at more positive potentials. Comparing this result with the coverages of adsorbed CN^{-} (fig. 2a), it is recognized that the surface oxidation proceeds in accordance with the desorption of CN⁻. In other words, adsorbed CN⁻ inhibits formation of an oxide layer up to 0.4 V. Taking into account that the oxidation of CN⁻ to OCN⁻ occurs in the potential region more positive than 0.4 V, the following oxidation processes can be considered:

(i) CN^- which covers the electrode surface desorbs and the oxidation of platinum surface occurs,

(ii) the surface oxygen atom reacts with CN^- to give OCN⁻, and the surface oxygen atoms are supplied by the dissociation of OH⁻ or H₂O molecules.

Fig. 3 shows the PM IRRAS spectra obtained for 0.1 mol/l KOCN and 0.1 mol/l KCl aqueous solution. The intense 2170 cm^{-1} band due to the OCN⁻¹ species in the solution is seen throughout the potential region. The PM IRRAS method should normally cancel the absorption signal from the bulk-phase species. The solution-phase species which is located at the double-layer region is subjected to the large electromagnetic field arising from the p-polarized light. Therefore, signals from the atmospheric vapor in the spectrometer or the bulk-phase solution in the electrochemical cell appear in the spectra owing to the imbalance of the p- and s-polarized signals. Weak bands due to the adsorbed OCN⁻ are seen in the $2240-2260 \text{ cm}^{-1}$ region together with the 2170 cm band. Hoffmann et al. have reported adsorbed OCNon an Au electrode which absorbs radiation at 2140 cm⁻¹ [12], whereas Corrigan and Weaver have

We have independently calculated the molecular orbitals for OCN^- (STO-3G), and found that the antibonding orbital of nitrogen lone pair lies just below the HOMO.



Fig. 3. Change in the PM IRRAS spectrum for 0.1 mol/ ℓ KOCN in 0.1 mol/ ℓ KCl aqueous solution as a function of the electrode potential.

reported absorbed OCN- on an Ag electrode which absorbs radiation at 2170 cm^{-1} [13]. However, the CN stretching frequency of the OCN_{ad} in the present work is slightly higher than those on the Au and Ag electrodes. When OCN- adsorbs on the electrode two types of orientation have been suggested: a flat orientation which interacts with π orbitals (highest occupied molecular orbital [10] (see footnote [‡])) and terminal coordination [14] with a nitrogen lone pair (closely spaced with the HOMO [10]). The molecular axis of the former species is parallel to the surface and is infrared-inactive because of the surface selection rule. Previous studies of bulk phase Pt(II)-cyanate complexes have indicated that the cyanate ligand was bonded exclusively through its nitrogen atom [15]. In addition, it has been shown that the OCN⁻ anion only chemisorbs at the N center from a calculation of the reaction potential map [16]. Therefore, the bands observed at 2240-2260 cm⁻¹ can be attributed to terminal surface-coordinated OCN⁻ species through the nitrogen atom. The higher frequency shift in the ν_{CN} frequency from its bulk value, 2170 cm^{-1} , is explained by the strengthening of the CN bond due to donation of the antibonding lone pair orbital, as in the case of CNadsorption. The intensity of the band grows with continuous frequency shift against the positive potential sweep up to 0.4 V, indicating increased donation, while the band center position does not shift at all at more positive potentials, where the oxidation reaction occurs steadily. This result shows that the linearly adsorbed OCN⁻ combines with a proton to give an HNCO molecule on the electrode, as shown in reaction (2).

3.2. Oxidation in methanol solution

The oxidation of CN^- and OCN^- in non-aqueous solvents is also examined. The IRRAS spectra in 0.01 mol/ ℓ KCN and 0.1 mol/ ℓ LiCl methanol solutions show that no signal was observed during the anodization except for the 2080 cm⁻¹ band of the bulk-phase CN⁻ species. The corresponding PM IRRAS spectra present the only peak due to the adsorbed cyanide group. The results indicate that oxidation does not occur in the observed potential region and that formation of OCN⁻ requires a hydroxyl ion produced by the dissociation of water.

As for the KOCN methanol solution, however, a further anodic reaction occurred. Fig. 4 shows the IRRAS spectra obtained for 0.01 mol/ ℓ KOCN and 0.1 mol/ ℓ LiCl methanol solutions. The bands at 2258 and 2342 cm⁻¹ are due to HNCO and CO₂, respectively. In contrast to the case in aqueous solution, the intensity of the HNCO band is much higher than that of CO₂. The appearance of the minor product CO₂ might be due to water impurity in methanol. Hydrogen could be supplied by dissociation of methanol and reaction (2) followed by the OCN⁻ adsorption dominated on the Pt electrode surface.

The HNCO molecule mentioned is unstable, and the 2258 cm^{-1} band disappears in a few minutes. This is suggestive of the existence of a further anodic reaction process. Parker and Burgert have reported



Fig. 4. Change in the IRRAS spectrum for 0.01 mol/l KOCN in 0.1 mol/l LiCl methanol solution.

the electrosynthesis of methyl carbamate using KOCN and methanol [17]. In order to elucidate the final product, we performed an IRRAS experiment in the 2000–1000 cm⁻¹ region. Three new bands were observed in the potential region more positive than

0.8 V at 1730, 1355 and 1260 cm⁻¹, which can be attributed to the C–O stretching, N–C stretching and C–O stretching vibrations of methyl carbamate, respectively. Therefore, methyl carbamate is the final product in methanol solution.

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