CROATICA CHEMICA ACTA CCACAA **51** (3) 243—247 (1978)

CCA-1117

YU ISSN 0011-1643
541.138
Original Scientific Paper

An Investigation of the Electrochemical Reactions of a Nickel Cyanide Complex at Mercury Electrode by Cyclic Voltammetry

D. Čukman and V. Pravdić

Laboratory of Electrochemistry and Surface Phenomena, »Ruđer Bošković« Institute, 41001 Zagreb, Croatia, Yugoslavia

Received June 16, 1978

Cyclic voltammograms obtained for the reduction and reoxidation reactions of nickel cyanide complex with and without an excess of free cyanide in solution are shown and discussed. These reactions could best be described as an ECE mechanism, accompanied by a fast equilibrium disproportionation reaction between the two Ni(I) complex intermediates.

INTRODUCTION

In a preceding communication[1] the results of investigation of electrochemical reactions of nickel cyanide complexes at mercury electrodes by cyclic chronopotentiometry were described. In brief, the results indicated divergence with data in literature[2,3], which postulated two sequential electron transfer steps with the electro-inactivation of both the intermediate and the final reduced form of the Ni(0) cyanide complex by two different independent chemical reactions. On the basis of diagnostic criteria developed for cyclic chronopotentiometry[4], it has been found, that the reduction and reoxidation reactions can best be described by an ECE mechanism, accompanied by a fast equilibrium disproportionation reaction between the two Ni(I) complex intermediates. The results are strictly valid only for the supporting electrolyte containing an excess of free cyanide, and the mechanism can be written as:

$$\mathrm{Ni(CN)_4^{2-}} \xrightarrow{e^-} \mathrm{Ni(CN)_4^{3-}} \tag{1}$$

$$\mathrm{Ni(CN)_4^{3-}} \xrightarrow{k_c} \mathrm{Ni(CN)_3^{2-}} + \mathrm{CN^-} \tag{2}$$

$$\mathrm{Ni(CN)_3^{2-}} \xrightarrow{e^-} \mathrm{Ni(CN)_3^{3-}} \tag{3}$$

$$\mathrm{Ni(CN)_4^{3-}} + \mathrm{Ni(CN)_3^{2-}} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{Ni(CN)_4^{2-}} + \mathrm{Ni(CN)_3^{3-}} \tag{4}$$

with the equilibrium constant defined as $K = k_f/k_b$.

It has been found by digital simulation and curve fitting, that for solutions with an excess of free cyanide $k_c = 0.34\ \mathrm{s^{-1}}$ for $10 < K < 100$. For solutions without excess cyanide, $k_c = 0.03\ \mathrm{s^{-1}}$, and $K = 10^{-3}$.

The analysis of cyclic chronopotentiometric data in solutions containing no free cyanide ion is marred by the problem of two reoxidation waves. In that case the quantitative evaluation of rate coefficients and numerical modelling becomes too involved or impossible. Also, the recombination reaction of the chemical step in the ECE mechanism is a second order reaction. Whether or not the analogy between solutions containing free cyanide and those without it can be accepted, has largely been left unresolved. It is the aim of this paper to substantiate the claim[1] that the mechanism of reduction and reoxidation reactions is basically the same in both solutions and that divergencies are limited to different reaction orders and rate coefficients of the chemical step alone.

EXPERIMENTAL

Experiments were done using a hanging mercury drop electrode of the Kemula type[5]. A platinum counterelectrode and a saturated calomel reference electrode were used in a conventional cell. Measurements were done using a PAR Model 174 Polarographic Analyzer with manual switching at predetermined potentials. Scan rates of 10 to 100 mV/s were used. Cyclic voltammograms were recorded on a Hewlett--Packard Model 7004B X-Y recorder.

$Ni(CN)_4^{2-}$ complex solutions were prepared by dissolving $K_2Ni(CN)_4$, prepared from $NiSO_4$ and KCN[6]. In these experiments only two solutions were used, both 1.06×10^{-3} mol dm^{-3} in $Ni(CN)_4^{2-}$. The supporting electrolyte in the first case, with an excess of free cyanide was 0.1 mol dm^{-3} KCl + 0.1 mol dm^{-3} KCN, the other solution was 0.1 mol dm^{-3} KCl only. pH was adjusted to 9.0 by titrating with KOH if necessary.

RESULTS AND DISCUSSION

Figure 1. shows the cyclic voltammogram obtained for the solution with an excess of free cyanide. The scan rate was 100 mV/s. There is only one

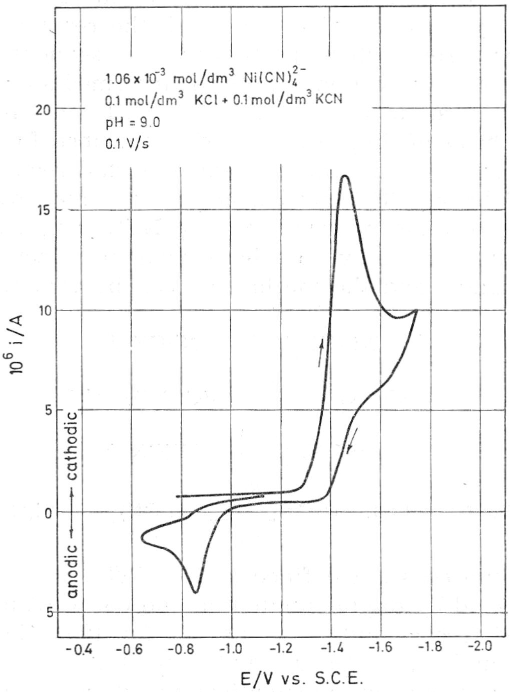

Figure 1. Cyclic voltammogram for 1.06×10^{-3} mol dm^{-3} $Ni(CN)_4^{2-}$ in 0.1 mol dm^{-3} KCN + 0.1 mol dm^{-3} KCl supporting electrolyte at pH = 9.0 and for the scan rate of 100 mV/s.

reduction and one reoxidation wave observed. The characteristic potentials are $E_{p/2} = -1400$ and $E_a = -850$ mV, respectively. The separation of the characteristic potentials indicate a highly irreversible electrochemical reaction.

Figure 2. shows the cyclic voltammogram for the solution without free cyanide, all other parameters being equal. In the first cycle a single cathodic peak and two anodic peaks are observed. In the second cycle a second cathodic peak is observed. It is suggested that this peak is the result of the more reversible second electron transfer reaction (3) in the ECE mechanism.

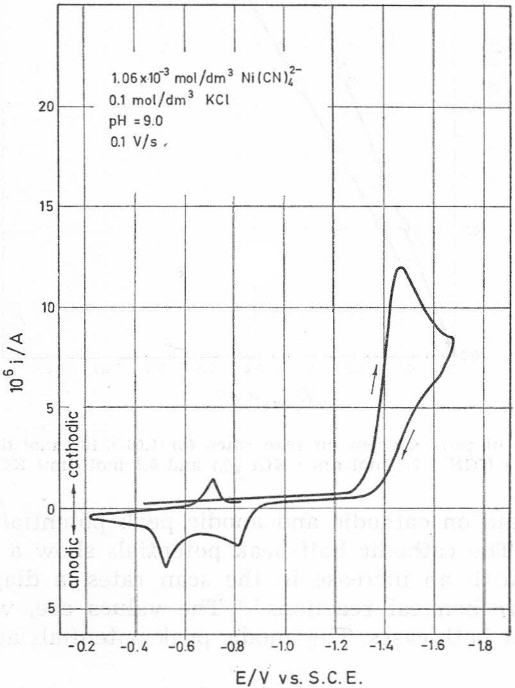

Figure 2. Cyclic voltammogram for 1.06×10^{-3} mol dm^{-3} $Ni(CN)_4^{-2}$ in 0.1 mol dm^{-3} KCl supporting electrolyte (no excess cyanide) at pH = 9.0 and for the scan rate of 100 mV/s.

The existence of $Ni(CN)_3^{2-}$ intermediate in kinetically significant concentration is the result of the slow recombination reaction (2) seen as:

$$Ni(CN)_3^{2-} + CN^- \rightarrow Ni(CN)_4^{3-}$$

which, due to the lack of excess free cyanide in solution, is a second order reaction. Here the cathodic and anodic peaks are separated by 600 mV, only slightly more than in the former case.

Figure 3. shows the dependence of the peak current for the cathodic wave upon the square root of the scan rate. A constant slope is a strong indication against either a preceding chemical step or a catalytic mechanism.[7,8] A slightly lower slope in solutions containing no free cyanide can be again interpreted as the inhibition of reaction (2). This assumption is also supported by the higher peak current values observed in solutions containing free cyanide, due to the fast regeneration of the original reactant complex.

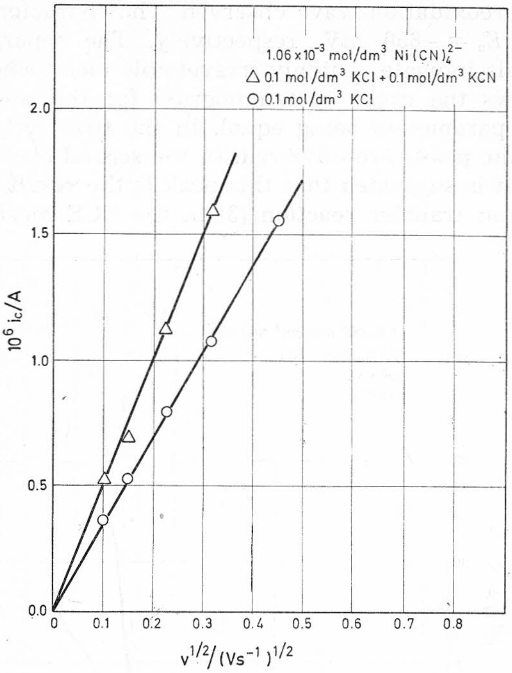

Figure 3. Dependence of peak current on scan rates for 1.06×10^{-3} mol dm^{-3} Ni(CN)$_4^{2-}$ in 0.1 mol dm^{-3} KCN + 0.1 mol dm^{-3} KCl (△) and 0.1 mol dm^{-3} KCl (○).

In Table I data on cathodic and anodic peak potentials and peak current ratios are given. The cathodic half-peak potentials show a shift towards more negative values with an increase in the scan rates, a diagnostic criterion of irreversible electrochemical reactions.[7,8] The values are, within experimental error, identical for both cases. The anodic peak potentials are more positive for

TABLE I

Cathodic and Anodic Peak Potentials and Peak Current Ratios for Different Scan Rates and Supporting Electrolytes for 1.06×10^{-3} mol dm^{-3} Ni (CN)$_4^{2-}$, pH = 9.0

Electrolyte mol dm^{-3}	v mV/s	$E_{p/2}$ (cat.) mV	E_p (anod.) mV	i_a/i_c
0.1 KCN + 0.1 KCl	10	— 1370	— 870	0.17
	20	— 1370	— 860	0.23
	50	— 1390	— 850	0.25
	100	— 1400	— 850	0.27
0.1 KCl	10	— 1390	— 820*	0.10
	20	— 1390	— 800*	0.13
	50	— 1380	— 810*	0.15
	100	— 1400	— 800*	0.17
	200	— 1420	— 780*	0.18

* potentials of the first anodic peak

solutions containing no excess cyanide. In this solution the observed differences could be interpreted as a result of peak separation for the anodic electron transfer reactions due to inhibition of reaction (2). However, it is difficult to account for the observed difference of 50 mV between both solutions, except by postulating the adsorption of free cyanide at the mercury electrode for which no experimental proof exists. This adsorption has been invoked before to facilitate electron transfer by a ligand bridging mechanism.[9]

The ratios of anodic to cathodic peak currents are well below 1, in accordance[7,8] with the observed irreversibility of the electron transfer reactions. In both cases the ratio increases with increasing scan rates: although not proving it, this result does conform with the hypothesis that the rate determining step is in the chemical reaction (2) of the ECE mechanism.

Acknowledgment. This work has been supported in part through Grant GF-31530 (P. L. 480) from the National Science Foundation, Washington, D. C. USA, and in part by a grant from the *Self-managing Authority for Scientific Research, SR of Croatia.* Extracted in part from the Ph. D. Thesis of D. Č., Univ. of Zagreb 1975.

REFERENCES

1. D. Čukman and V. Pravdić, submitted for publication to *J. Electroanal. Chem.*
2. A. A. Vlček, *Collect. Czech. Chem. Commun.* **22** (1957) 984.
3. A. A. Vlček, *Collect. Czech. Chem. Commun.* **22** (1957) 1736.
4. H. N. Blount and H. B. Herman, *J. Electrochem. Soc.* **117** (1970) 504.
5. W. Kemula and Z. Kublik, *Anal. Chim. Acta* **18** (1958) 104.
6. *Inorganic Syntheses,* Vol. II, W. C. Fernelius (Ed.) McGraw-Hill, New York 1946.
7. R. S. Nicholson and I. Shain, *Anal. Chem.* **36** (1964) 706.
8. E. R. Brown and R. F. Large, *Cyclic Voltammetry, AC Polarography and Related Techniques,* in: A. Weissberger and B. R. Rossiter (Eds.), *Physical Methods of Chemistry,* Vol. IIA, Wiley-Interscience, New York, 1971, Ch. VI. pp. 423—531.
9. J. Heyrovsky, *Discuss. Faraday Soc.* **1** (1947) 212.

SAŽETAK

Istraživanje elektrokemijskih reakcija nikal-cijanidnog kompleksa na živinoj elektrodi cikličkom voltametrijom

D. Čukman i V. Pravdić

Pokazani su ciklički voltamogrami redukcije i reoksidacije nikal-cijanidnog kompleksa u prisutnosti i odsutnosti slobodnog cijanid-iona u otopini. Iako se u slučaju suviška cijanid-iona u otopini pojavljuje samo jedan anodni val, a u odsutnosti dva, pokazano je da se u oba slučaja može prihvatiti kao valjan model ECE mehanizma sa pratećom reverzibilnom disproporcionacijom nikal(I)-kompleksa. Razlike u vrijednostima potencijala katodnog vala ($E_{p/2}$) i anodnog (E_a), kao i različiti odnosi struje vrha anodnog vala prema struji vrha katodnog vala pripisuju se utjecaju cijanid-iona na kinetiku kemijske reakcije C, u ECE mehanizmu.

LABORATORIJ ZA ELEKTROKEMIJU
I POVRŠINSKU KEMIJU
INSTITUT »RUĐER BOŠKOVIĆ«, ZAGREB

Primljeno 16. lipnja 1978.