CARBON PASTE ELECTRODES APPLICATION TO CATHODIC REDUCTIONS AND ANODIC STRIPPING VOLTAMMETRY

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The value of carbon paste electrodes for anodic oxidations has been firmly established[1-3]. Since this electrode material showed a considerable hydrogen overpotential, the potentialities for cathodic reductions were investigated in detail. The results were most promising and establish carbon paste as a practical, dual-purpose electrode material. Nujol pastes, as described previously, were used in this study. Such electrodes are designated CE-NjP[3].

(A) *Cathodic range and residual currents*

Current-voltage curves were run in a variety of supporting electrolytes to establish the usuable cathodic potential range over which the CE-NjP could be used. Fig. 1 shows typical results. The greatest range is, of course, obtained in neutral and basic

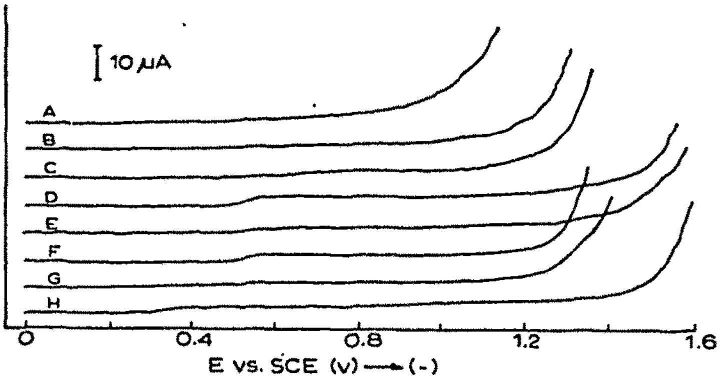

Fig. 1. Typical cathodic background runs for CE-NjP.
A. 1 *M* perchloric acid;
B. 1 *M* hydrochloric acid;
C. 1 *M* sodium acetate-acetic acid;
D. 1 *M* sodium perchlorate;
E. 1 *M* potassium chloride;
F. 1 *M* potassium nitrate;
G. 1 *M* ammonia-ammonium chloride;
H. 1 *M* sodium hydroxide.

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media. In general, the cathodic range extends to *ca.* —1.2 to —1.4 V *vs.* S.C.E., excluding strong acid media. This, of course, is not as great as mercury, but is a decided improvement over noble metals.

However, a relatively small but non-removable residual current is found on the cathodic side with the CE-NjP. This can be seen in Fig. 1 as the small wave between —0.4 and —0.6 V. This is a marked contrast to the anodic residual current which is almost nil up to the onset of background oxidation. Attempts to remove this residual current completely were not successful. It appears to be an oxygen wave, as suggested by the pH dependence and the fact that it decreases significantly on thorough deaeration. It was reasoned that it was due to oxygen in the paste itself which obviously could not be removed completely by solution deaeration. Accordingly, the Nujol was deaerated before mixing, and, in other attempts, the carbon was degassed and then an attempt made to sorb nitrogen on the carbon at low temperatures. None of these treatments (in addition to others) *completely* eliminated the residual current and it is believed that the mixing process which obviously is most conveniently done in the ordinary atmosphere would re-introduce oxygen in the paste even after the most careful removal.

Fortunately, the residual wave has a very flat plateau and it was found that cathodic reductions could be carried out "on top" of this wave, *i.e.*, using it as a base line for peak current measurements. In fact, although low level determinations are difficult by direct cathodic reduction, otherwise the residual current is not troublesome at all. All electroactive species studied were 10^{-3} *M* or greater in concentration.

(*B*) *Reduction of metal ions*

Figure 2 illustrates analytical results for the reduction of cadmium (II) in 1 *M*

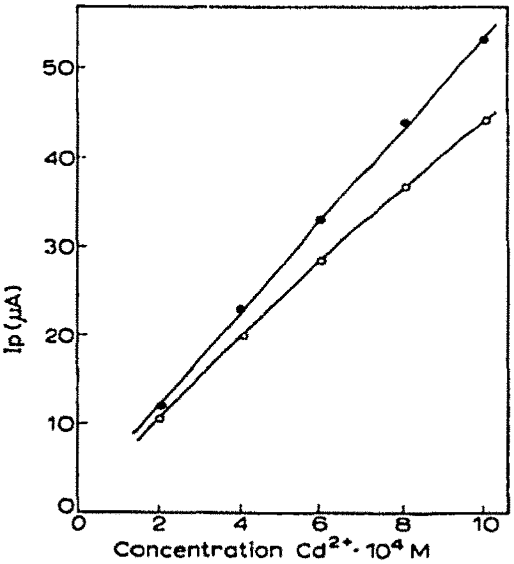

Fig. 2. Peak current *vs.* concentration for cadmium(II) reduction.
○ Experimental currents,
● Corrected for *iR*.

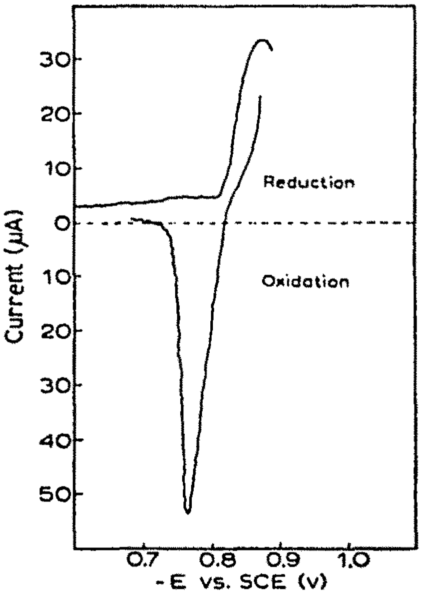

Fig. 3. Reduction and anodic stripping of thallium(I). $1 \cdot 10^{-3}$ *M* Tl(I) in 1 *M* ammonia–ammonium chloride.

potassium chloride as an example of a reduction carried out "on top" of the residual current. The lower line is for data directly from a Leeds and Northrup Electrochemograph with a scan rate of 200 mV/min. The upper curve represents the peak currents corrected for *iR* drop by the method of DELAHAY AND STIEHL[4]. Either line functions satisfactorily as a working curve but the advantages of a controlled potential polarograph are obvious. Satisfactory results similar to that of Fig. 2 were obtained for other metal ion systems.

In all metal ion reductions, anodic stripping procedures were checked. That most of the reductions involved deposition as the metal was evident from the fact that the

TABLE I

REDUCTION OF METAL IONS AT STATIONARY CE-NjP ELECTRODES

Electroactive species	*Medium*	$E_{p/2}$ *(V vs. S.C.E.)*
Bismuth(III)	*M* $HClO_4$	(−) 0.19
	M $NaClO_4$	0.25
	M HCl	0.19
	M KNO_3	0.12
	M NaAc–*M* HAc	0.32
Tin(II)	*M* HCl	0.57
	M $HClO_4$	0.54
	M $NaClO_4$	0.61
Cadmium(II)	*M* $HClO_4$	0.88
	M HCl	0.84
	M KCl	0.84
	M $NaClO_4$	0.78
	M NH_4Cl–*M* NH_4OH	0.99
	M NaAc–*M* HAc	0.86
Load(II)	*M* $NaClO_4$	0.53
	M $HClO_4$	0.56
	M HCl	0.56
	M KNO_3	0.53
	M NaAc–*M* HAc	0.61
Cobalt(II)	*M* NH_4Cl–*M* NH_4OH	0.98
	M $NaClO_4$	0.82
Iron(II)	*M* KCl	0.99
	M $NaClO_4$	0.98
Copper(II)	*M* $HClO_4$	0.23
	M HCl (2nd wave)	0.46
	M KCl (1st wave)	0.20
	M KCl (2nd wave)	0.40
	M NH_4Cl–*M* NH_4OH (1st wave)	0.18
	M NH_4Cl–*M* NH_4OH (2nd wave)	0.67
Thallium(I)	*M* $HClO_4$	0.83
	M HCl	0.83
	M $NaClO_4$	0.84
	M KCl	0.84
	M NH_4Cl–*M* NH_4OH	0.83
Nickel(II)	*M* KNO_3	0.97

anodic peak current (i_p) was far greater than that expected if the re-oxidation process involved a solution component. Further, after reduction, the solutions were stirred to destroy any concentration gradients at the electrode before re-oxidation. Figure 3 shows a typical example of a cathodic reduction and the corresponding anodic stripping for thallium in an ammonia–ammonium chloride buffer. No attempts were made to carry out extensive quantitative studies of the anodic stripping. The theory and utility of such processes is well established and applications are straightforward. Obviously, for metal ions, the use of anodic stripping completely eliminates any worry about the carbon paste residual current while, at the same time, it affords far greater sensitivity.

Table I summarizes the $E_{p/2}$ values for some typical metal ion reductions in a variety of background electrolytes. Specific points of interest on the individual systems are discussed briefly below.

Bismuth(III). In general the reproducibility of i_p for bismuth(III) reductions was good in all media. However, when the same electrode surface was used for several runs, the $E_{p/2}$ tended to shift slightly and then become stabilized. This shift in perchlorate media was toward more cathodic potentials but toward anodic values in hydrochloric acid. Excellent stripping patterns were obtained in perchlorate, chloride and acetate media.

Tin(II). The reduction of tin(II) in 1 *M* hydrochloric and perchloric acids and 1 *M* sodium perchlorate was successful. However, no reduction was obtained in 1 *M* sodium hydroxide. Satisfactory stripping patterns were obtained in both chloride and perchlorate backgrounds.

Cobalt(II). The reduction of cobalt(II) was possible in 1 *M* sodium perchlorate, 1 *M* potassium chloride, and ammonia-ammonium chloride medium but no reduction waves were obtained in 1 *M* hydrochloric or perchloric acids.

The shape of the cobalt(II) reduction wave was very non-reproducible. Anodic strippings in both ammoniacal and perchlorate media verified metal deposition.

Iron(II). Iron(II) could be reduced in 1 *M* potassium chloride, 1 *M* sodium perchlorate and 0.2 *M* sodium sulfate media. In all three supporting electrolytes, anodic stripping patterns confirmed the presence of deposited metal.

Nickel(II). Nickel ion reduction is one of the most interesting studies at the carbon paste electrode. A well-defined reduction peak was obtained in 1 *M* potassium nitrate. After deposition, the electrode was removed from solution, rinsed with distilled water and anodically stripped into sodium acetate containing dimethylglyoxime. No red color appeared until the potential necessary for stripping was applied showing definitely the metal had been deposited.

The interesting feature of the nickel(II)–nickel metal system is the extremely large degree of irreversibility. Thus, the $E_{p/2}$ for reduction is −0.97 V *vs.* S.C.E. The anodic stripping occurs at about +1.0 V *vs.* S.C.E. — about 2 V between the two processes. Clearly such an observation would be difficult to make at any other electrode.

The reductions of cadmium(II) and lead(II) were conventional in all respects and copper(II) showed stepwise reduction to copper(I) and the metal.

A comparison of $E_{p/2}$ values at the CE-NjP with $E_{1/2}$'s at the D.M.E. afford some interesting observations. In nearly all cases the $E_{p/2}$ for a given metal ion reduction at CE-NjP is different from that at the D.M.E., as well could be expected. For thallium(I), cadmium(II), and lead(II), the reduction is at more cathodic potentials for CE-NjP. However, cobalt(II) and iron(II) deposit at more anodic potentials on carbon paste. It is interesting to note that the former group of metals readily form amalgams with mercury while cobalt(II) and iron(II) do not form amalgams readily. Further interpretation of such results must await more careful studies of these and other metal ion systems.

Although metal ion reduction potentials at carbon paste differ from those at the D.M.E., they are relatively reproducible and in no way hamper analytical applications. It is safe to conclude that a number of metal ions can be determined successfully at the CE-NjP either by cathodic reduction or anodic stripping. If one examines all the metal ions studied herein, a reproducibility of ± 20 mV is the best that can be claimed for $E_{p/2}$ values. Thus for analytical work the anodic stripping technique would be recommended.

(C) *Organic reductions*

The cathodic range of the CE-NjP obviously will not allow as wide a spectrum of organic reductions to be accomplished as is possible with the D.M.E. However, determinations of easily reducible groups like the nitro function are quite possible. To indicate the potential scope, Table II shows results on a variety of aromatic and aliphatic nitro compounds. In almost all cases, as was expected, the reductions were irreversible, but the peak polarograms were well defined and suitable for analytical determinations.

TABLE II

REDUCTION OF NITRO COMPOUNDS AT STATIONARY CE-NjP ELECTRODES

Electroactive species	*Medium*	$E_{p/2}$ (*V vs. S.C.E.*)
p-Nitrodimethylaniline	*M* HCl	(−) 0.38
p-Chloronitrobenzene	*M* HCl	0.42
p-Nitrostyrene	*M* HCl + acetone	0.32
p-Nitrobenzoic acid	*M* HCl	0.29
Nitrocyclohexane	*M* HCl	0.87
1-Nitropropane	*M* HCl	0.92
2-Nitropropane	*M* HCl	1.00
Nitrodiphenyl	*M* HCl + acetone	0.43

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SUMMARY

The utility of carbon paste electrodes for metal ion reductions and anodic stripping voltammetry is demonstrated. In addition certain organic reductions can be accomplished. Extension of the use of carbon electrodes to the cathodic range shows that this electrode has a wide range of potential applications. For anodic oxidations, the carbon paste electrode is perhaps the most versatile and useful stationary electrode available; it possesses practically zero anodic residual current and readily reproducible surfaces, and is simple to prepare and use. On the cathodic side carbon pastes are limited by a non-removable residual current but this difficulty seems readily circumvented.

RÉSUMÉ

Les électrodes en pâte de carbone conviennent très bien pour les réductions d'ions métalliques et pour la voltammétrie anodique ("stripping voltammetry"). En plus, certaines réductions organiques peuvent être affectuées. Ces électrodes présentent de nombreux avantages: un courant résiduel anodique pratiquement nul, des surfaces bien reproductibles; d'autre part, elles sont faciles à préparer.

ZUSAMMENFASSUNG

Es wird gezeigt, dass sich Kohlenpaste-Elektroden für die Reduktion von Metallen und anodische "stripping" voltammetrie sehr gut eignen. Ausserdem können damit Reduktionen gewisser organischer Verbindungen erzielt werden. Kohlenpaste-Elektroden zeigen im kathodischen Bereich eine weite Anwendungsmöglichkeit. Sie zeigt praktisch keinen anodischen Reststrom, besitzt eine gut reproduzierbare Oberfläche und ist leicht herzustellen. Ihre Anwendung als Kathode ist etwas begrenzt wegen einem nicht entfernbaren Reststrom.

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