

On the behaviour of the dry cell graphite electrode

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Abstract. It is reported that for staircase voltammetric work, a dry cell graphite electrode after wax impregnation and polishing, behaves as well as a glassy carbon electrode.

Keywords. Graphite electrode; staircase voltammetry; glassy carbon substitute.

1. Introduction

The ubiquitous dry cell has made the embedded graphite rod one of the most easily and widely available materials. If extracted from a discharged dry cell, the rod is virtually zero-cost. It was natural to investigate the use of such a cheap material as an electrode for student laboratories (Natarajan and Subramanian 1976). The dry cell graphite (DCG) electrode has indeed been found to be quite reliable for potentiometric measurements in acid–base and redox systems (Bhattacharjee *et al* 1981; Rao and Waddington 1982). It was therefore felt that the utility of a DCG electrode for voltammetry should be examined. This note describes the preliminary results of such an investigation.

2. Approach

Platinum has always been regarded as a near-perfect electrode for potentiometric measurements but has limited use in voltammetry due to oxide layer formation. In recent years (Hu *et al* 1985; Thornton *et al* 1985), it has been established that the performance of a glassy carbon (GC) electrode is almost as satisfactory. We have therefore used the GC electrode (from Sigri Electrographit) as the standard for evaluating the quality of the DCG electrode. The comparative data that have been obtained include equilibrium and non-equilibrium parameters for an inorganic as well as an organic system. Since a raw DCG electrode is found to be unsatisfactory (stability and reproducibility are the major drawbacks), the electrode has been subjected to different types of treatment (e.g. thermal, chemical, mechanical etc.) and electrochemical parameters have been measured to monitor the electrode at various stages of treatment.

3. Procedure

The central graphite rod of a discharged dry cell was extracted and used as the starting

material. Earlier work (Bhattacharjee *et al* 1981) has shown that such an electrode has an unstable response; it is therefore cleaned. Two types of treatments were given: In the first treatment, electrodes were cleaned with sand paper followed by heating on a flame to remove volatile impurities. They were then placed in 0.5 M $K_2Cr_2O_7$ solution in 2 M H_2SO_4 for about 12 h. In the second, electrodes were cleaned with sand paper, heated as before and then washed continuously in a Soxhlet apparatus by a hot azeotropic mixture of hydrochloric acid and water. The extract coming out of the powder was tested for Fe^{3+} ion periodically. After about 48 h, no significant amount of iron (the major impurity) was detected. Both the procedures yield identical electrodes as far as potentiometric and voltammetric measurements are concerned. The resulting electrode has a stable, reproducible potential in a potentiometric set-up. However, in cyclic voltammetric measurements, this electrode yields a value of the residual current much higher than that observed with a GC electrode. In fact, the value is high enough to preclude the use of this type of DCG electrode for kinetic measurements. It may be recalled that a similar behaviour has been reported (Lord and Rogers 1954) for the spectroscopic graphite electrode, where the high residual current has been attributed to the high porosity. Since wax impregnation is known to reduce residual current (Elving and Smith 1960), the DCG electrode was impregnated with wax in the following manner.

A thick-walled test tube containing the wax (which is used to seal RF coils in a radio set) was placed in a container of boiling water. After the wax melted, the electrode was placed in the tube. The tube was then evacuated until no more bubbles arose from the electrode during the evacuation. The electrode was then removed from the wax and coaxial copper wire was tightened over it by another thick copper wire. Teflon tape was then wrapped over the electrode so that only the circular tip of the electrode is exposed to the solution. The tip was polished to a mirror finish by rubbing it over chamois leather.

The glassy carbon rod was force-fitted into a teflon rod and polished according to the reported procedure (Hu *et al* 1985).

For the purpose of convolution (Myland and Oldham 1988), weighting factors were calculated using a general recursion algorithm. In our case $\phi = 0.66$,

$$w_0 = \phi^{1/2},$$

$$W_j = \sum_{k=1}^j w_{j-k} \left[\left(\frac{\phi}{k-1+\phi} \right)^{1/2} - \left(\frac{\phi}{k+\phi} \right)^{1/2} \right],$$

and neopolarograms were generated using the following formula,

$$m_j = (\pi \Delta t)^{1/2} \sum_{j=1}^J w_{j-j} i_j,$$

where Δt (in seconds) is the width of a voltage step.

4. Results and discussion

The chemicals used were of AR grade and were used as such. Temperature in all measurements was maintained at 25°C. A saturated silver-silver chloride electrode and a platinum wire were used as reference and counter electrode respectively.

Table 1. Comparison of various graphite electrodes.

	Eveready				Philips (Chromic acid)	Nippo (Chromic acid)	Glassy carbon
	(Chromic acid) ^a		(Soxhlet apparatus)				
	1	2	3	4			
E_0 (mV) vs. saturated Ag, AgCl electrode	219	218	219	216	218	212	241
Slope (mV)	61.7	71.2	64.2	61.9	66.3	66.3	60.3
$K_0 \times 10^3$ cm/s	2.6	2.2	2.7	2.9	2.4	1.8	4.2

^a This refers to the method/reagent used for cleaning the graphite rod.

Potentiometric measurements were carried out in a mixture of potassium ferri/ferrocyanide solution to determine the standard electrode potential. They are shown in table 1.

A staircase voltogram (SCV) of 5 mM $K_3Fe(CN)_6$ and 1 M KCl was recorded on a home-made computerised electrochemical system (Srivastava and Upadhyay 1988). The instrument is built around a Z.80 microcomputer—"Color Genie". The instrument is memory-mapped into the unutilised address space which is mainly used for connecting a disk operating system. There are two main parts of the instrument, waveform programmer and data recording system. The waveform programmer is designed to generate essentially two types of waveforms – a sequence of straight line segments for cyclic voltammetry and a sequence of voltage steps for various types of pulse polarography. The data recording system is designed to record current data in a local 1 KB static RAM. At the end of the experiment, data are transferred into the computer for further processing. Assembly language programs have been written to perform cyclic voltammetry, staircase voltammetry, normal pulse polarography and differential pulse polarography. A print screen program has also been written to print voltograms using a dot-matrix printer.

Figures 1 and 2 show the SCV on a GC and a DCG electrode respectively. The forward sweep was convoluted in both cases to obtain a neopolarogram. They are shown in figures 3 and 4. The log plot of the neopolarogram gives the slope as $65.51 V^{-1}$ for the GC and as $54.68 V^{-1}$ for the DCGE. The intercept gives the half wave potential as 248 mV and 209 mV for GC and DCG electrodes respectively. This may be compared with the theoretical slope, $2F/RT (= 78.01 V^{-1}$ at $25^\circ C$). In as much as the slope of the log plot is a measure of the reversibility, the data shows the reversibility at a DCG electrode deviates as much from the value of a GC electrode as a GC electrode deviates from the ideal case.

Voltograms were recorded at various sweep rates and figure 5 shows the variation of cathodic peak potential with $\log v$ where v is the sweep rate. The heterogeneous rate constant (K_0) were evaluated by the critical sweep rate at which two straight lines intersect (Ferrier and Schroder 1973; Gileadi *et al* 1975; Seralathan *et al* 1987). Values of K_0 are listed in table 1.

Figures 6 and 7 show the SCV of 5 mM *p*-amino phenol in 0.05 M H_2SO_4 . In this solution both the electrodes show one oxidation and two reduction peaks as observed (Gileadi *et al* 1975) on a platinum electrode. Since a saturated Ag/AgCl reference electrode was used in 0.05 M H_2SO_4 , the peak potentials cannot be accessed due to the liquid junction potential but the nature of the mechanism of oxidation on

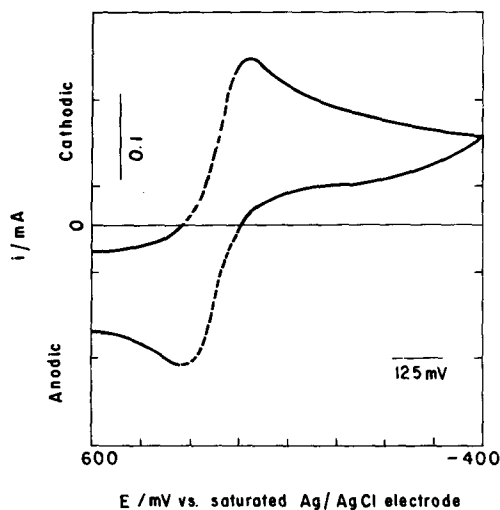


Figure 1. Staircase voltammogram at scan rate 100 mV s^{-1} of $5 \text{ mM K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl at a glassy carbon electrode.

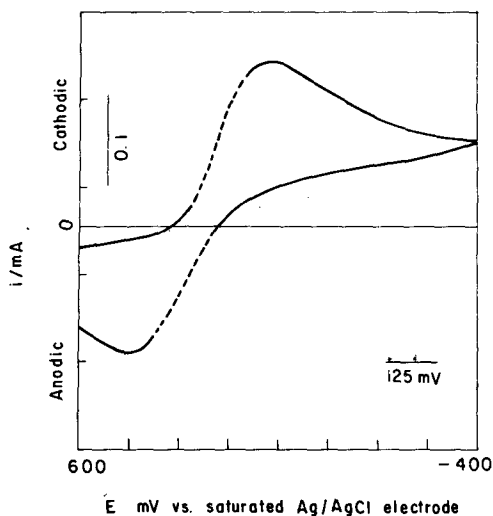


Figure 2. Staircase voltammogram at scan rate 100 mV s^{-1} of $5 \text{ mM K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl at a DCG electrode.

platinum, GC and DCG electrodes is similar as the number of peaks and their relative peak potentials remain the same.

Table 1 shows the comparative behaviour of different electrodes extracted from dry cells of different brands. Also included is the behaviour of electrodes from different dry cells of the same brand. Columns 1, 2, 3 and 4 of table 1 show that both the methods of cleaning yield identical electrodes. Perhaps chromic acid treatment cleans only the surface of the electrode which is just sufficient for potentiometry and voltammetry. Moreover the response of such electrodes is independent of battery brand. Differences in the internal constitution of different brands of dry cells are therefore of no

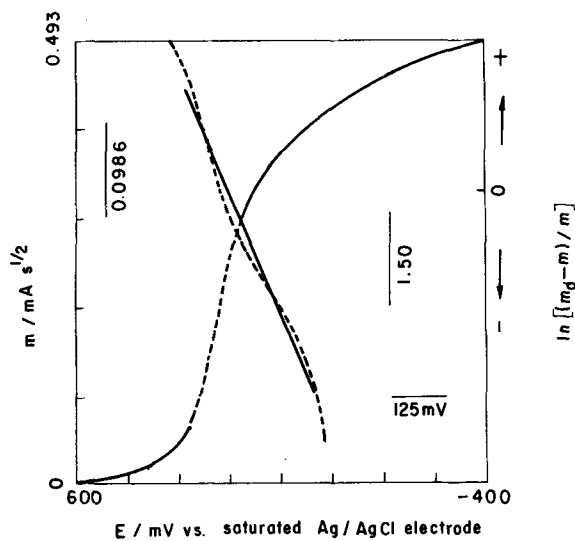


Figure 3. Neopolarogram of the convoluted data of the experiment shown in figure 1. The line is the best-fit regression line of data between 326.5 mV and 14.0 mV.

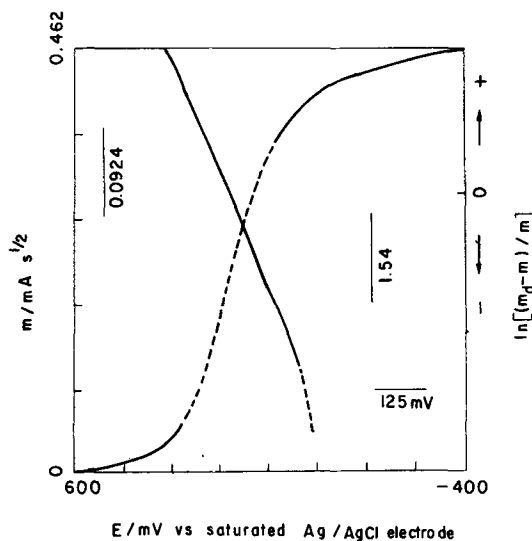


Figure 4. Neopolarogram of the convoluted data of the experiment shown in figure 2. The line is the best-fit regression line of data between 326.5 mV and 14.0 mV.

consequence as far as voltammetric measurements are concerned. In view of the easy availability of a DCG electrode and the rather simple procedure for its treatment, the close agreement observed with the GC electrode is quite remarkable.

The use of battery graphite (BC) powder (made by powdering graphite rods and cleaning them in a Soxhlet apparatus as described earlier) for making the so-called carbon paste electrodes is a possibility which needs further investigation. As is well-known, such electrodes are normally prepared from spectroscopic grade graphite

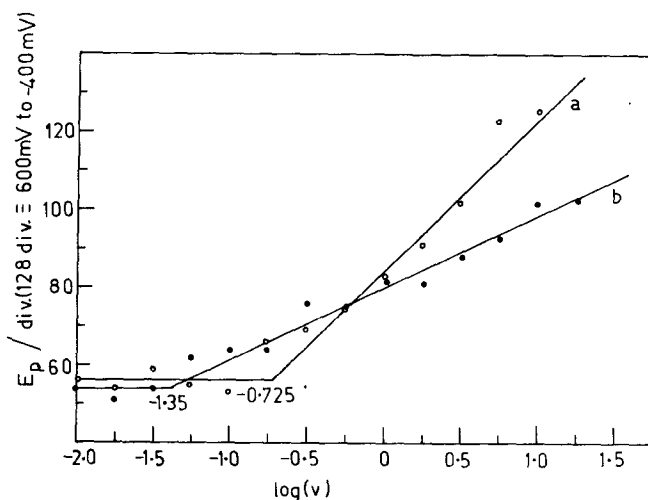


Figure 5. Variation of cathodic peak potential with $\log(v)$. Curve a is for the GC and curve b is for the DCG electrode.

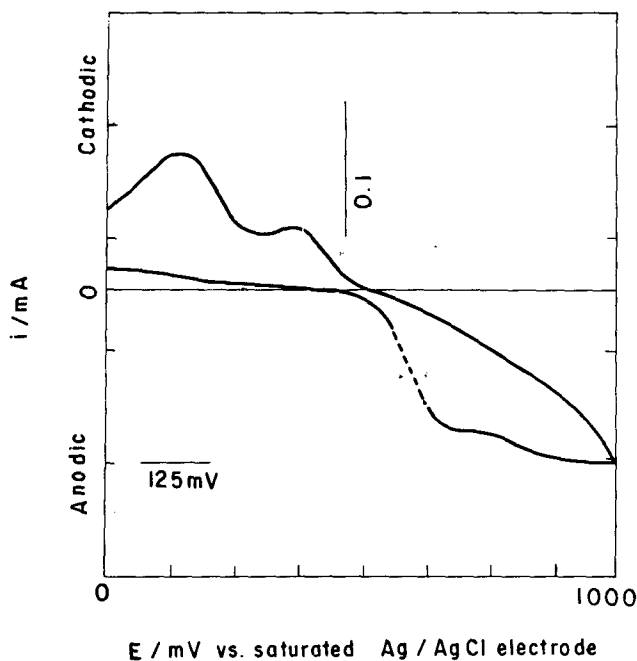


Figure 6. Staircase voltammogram at scan rate 100 mV s^{-1} of $5 \text{ mM } p\text{-amino phenol}$ in $0.05 \text{ M H}_2\text{SO}_4$ at a glassy carbon electrode.

powder by incorporating a complexing reagent or an ion exchange resin directly into the carbon powder paste (Hernandez *et al* 1988). Preliminary results with BC powder have been quite encouraging and further work is in progress to study the comparative selectivity and sensitivity of such electrodes *vis a vis* the electrodes made from spectroscopic grade graphite.

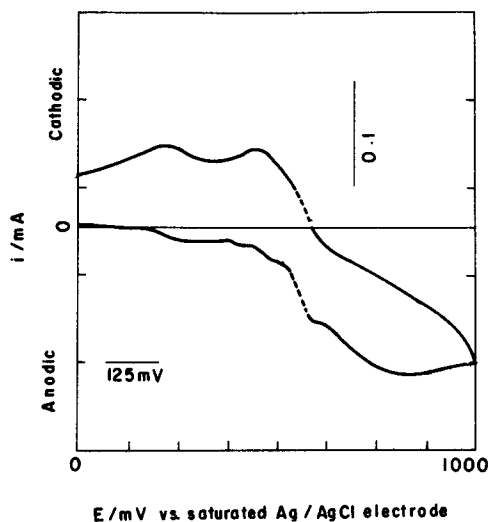


Figure 7. Staircase voltammogram at scan rate 100 mV s^{-1} of $5 \text{ mM } p\text{-amino phenol}$ in $0.05 \text{ M } \text{H}_2\text{SO}_4$ at a DCG electrode.

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