Carbon Film Resistors as Electrodes: Voltammetric Properties and Application in Electroanalysis

Christopher M. A. Brett,[*+] *Lúcio Angnes,*[++] and *Hans-Dieter Liess*[+++]

[+] Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal; e-mail: brett@ci.uc.pt
[++] Instituto de Química, Universidade de São Paulo, CP 26077, 05599-970 São Paulo – SP, Brazil
[+++] Institut für Physik, Fakultät für Elektrotechnik, Universität der Bundeswehr München, D-85577 Neubiberg, Germany

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Abstract

The voltammetric properties of electrodes made from carbon film resistors of 2 Ω have been studied and compared with those of commercially available glassy carbon, before and after electrochemical preconditioning in perchloric acid. The potential window and background currents have been measured in different aqueous solutions. Cyclic voltammetry of hexacyanoferrate(II) oxidation has been carried out and compared with glassy carbon and diamond film electrodes. Promising results have been obtained for the anodic stripping voltammetry of metal ions, particularly zinc ion, without interference from hydrogen evolution, and augurs well for substituting mercury electrodes in stripping analysis.

Keywords: Carbon film electrode, Carbon film resistor, Potential window, Anodic stripping voltammetry, Zinc

1. Introduction

Present trends in electroanalytical chemistry have included the development of new electrode materials for fast-response, selective electrochemical sensors for long-term use in real media with the minimum of pretreatment, and which are disposable or have easily renewable surfaces [1]. Within this broad area, there has been a search for new solid electrode materials with wide potential windows in order to extend the range of accessible applied potentials. Much of this effort has involved carbon-based materials, such as glassy carbon and carbon paste, which have already had much success in recent decades, particularly in the positive potential range for studying oxidations [2]. It has been discovered recently that glassy carbon doped with heteroatoms such as nitrogen, silicon and fluorine can improve the available potential window [3]. Additionally, boron-doped diamond electrodes have been developed which show a wide potential window in both the positive and negative directions [4, 5], as do electrodes of nitrogen-incorporated tetrahedral amorphous carbon [6].

A different approach is through using carbon film electrodes. These have been prepared by pyrolysis of an organic precursor and it was found that the positive potential limit is similar to that of other carbon electrodes [7]; they can be made sufficiently thin so as to be optically transparent [8]. Microelectrode arrays have been produced by this technique [9].

An important challenge in electroanalysis is to find a good replacement for mercury electrodes in the negative potential range, owing to concerns with its environmental toxicity. Carbon materials with a wide potential window are good candidates for this purpose. This has particular importance for stripping voltammetry applications where the preconcentration reduction step needs to be carried out at potentials which can approach −1.5 V (vs. saturated calomel electrode) in aqueous solution for zinc, or need to be even more negative for manganese ions [10]. As an alternative to liquid mercury electrodes – hanging or static drops – a number of electrode material substrates including glassy carbon electrodes have been used as substrates for thin mercury films formed prior to the electroanalytical determination or co-deposited with the cations of interest [11].

Much effort has been devoted to procuring other electrode materials with a high overpotential for the evolution of hydrogen. One approach has involved the use of thick graphite films which incorporate insoluble mercury salts such that mercury is formed on their surface when a sufficiently negative potential is applied [12–15]. Lead ions have recently been measured by differential pulse anodic stripping voltammetry at boron-doped diamond electrodes at sub-micromolar concentration levels following deposition at −1.0 V (vs. SCE) [16]. Preliminary results for the measurement of a mixture of zinc, lead and cadmium ions by linear sweep anodic stripping voltammetry have also been reported [17].

In this work, carbon film resistors have been made into electrodes and their potential range and voltammetric properties examined, particularly close to the limit of the negative potential range for application in stripping voltammetry.

2. Experimental

Electrodes were made from carbon film resistors (2 Ω nominal resistance). These resistors are fabricated from ceramic cylinders of length 1.1 cm and external diameter 0.3 cm by pyrolytic deposition of carbon. A quartz bottle is filled with the ceramic rods and is heated up in a furnace to 1100 °C. Then a continuous flow of nitrogen with a fraction of hydrocarbons (usually methane) is fed through the bottle, while turning the bottle round in order to give every rod the opportunity to be exposed to the pyrolytically decaying hydrocarbon gas. After 10 min to 1 h, depending on the desired thickness, a carbon layer of 5 to 500 Ω per square is obtained. Heating up and cooling down of the bottle contents is done in an atmosphere of nitrogen gas to avoid oxidation. For a 2 Ω carbon film resistor, the carbon film had a thickness of ca. 15 μm as measured by cross-section measurements after embedding in epoxy resin. A tight-fitting metal cap is then placed over each end with the external faces acting as a gold external contact at each end.

To make the electrodes, a thin conducting wire was joined to one of the two gold contacts with silver conducting paint and the

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two contacts were then protected by normal epoxy resin. In this way the electrode geometric area was ca. 0.7 cm^2.

Measurements were made in a one-compartment voltammetric cell containing a platinum foil auxiliary electrode and a saturated calomel electrode (SCE) as reference. Voltammetric experiments were carried out using either a PAR 273A potentiostat (EG&G, Princeton, NJ) with M270 research electrochemistry software and M271 cool kinetic analysis software or with a µAutolab potentiostat (Eco Chemie, Utrecht, The Netherlands) controlled by GPES 4.5 software. Capacitances were determined from impedance spectra recorded on a Solartron 1250 frequency response analyzer coupled to a 1286 electrochemical Interface.

All solutions were made from analytical grade reagents and Milli-Q ultrapure water (resistivity $\geq$ 18 MΩ cm). Stock solutions of supporting electrolyte and of 1 mM zinc nitrate were prepared and diluted as appropriate with supporting electrolyte. Solutions of 1 mM potassium hexacyanoferrate(II) were prepared on the day of use by dissolution of the salt in the supporting electrolyte. Experiments were carried out at room temperature (25 ± 1°C) with or without the removal of oxygen, by bubbling nitrogen through the solutions.

After preliminary experiments, to be described below, an electrochemical activation procedure was used in all subsequent studies. This involves cycling the new electrodes 3 times in 1.0 M perchloric acid solution between limits defined by a maximum current of ± 1 mA at a scan rate of 100 mV s^{-1}.

In anodic stripping voltammetry experiments, the metal ions of interest were preconcentrated directly on the carbon film surface by electrodeposition and then stripped by a positive square-wave voltammetric potential scan. In the case of zinc ion, deposition was carried out at -1.55 V (vs. SCE) and square-wave parameters were: frequency 25 Hz, scan increment 1 mV, amplitude 20 mV, the scan commencing at -1.5 V (vs. SCE).

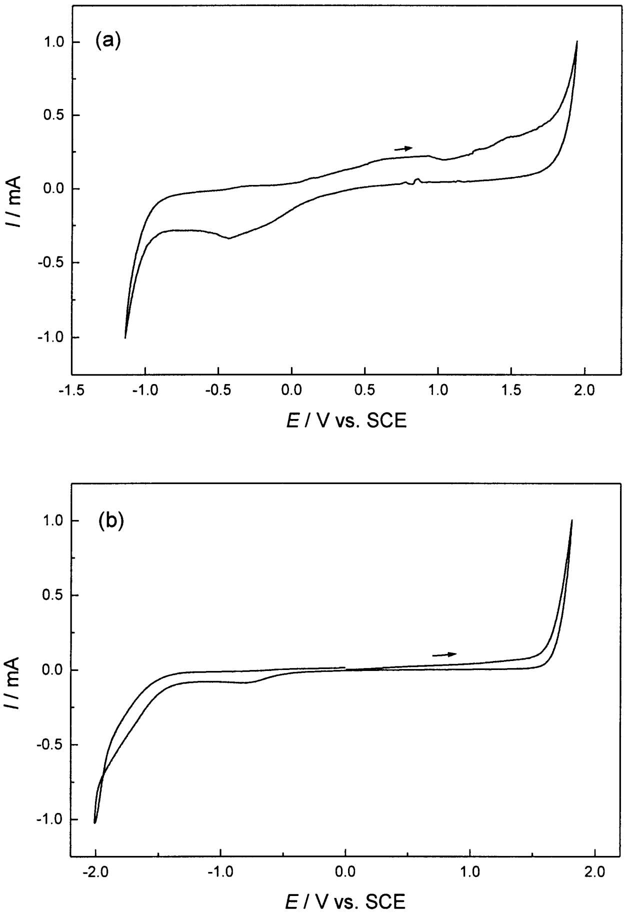

Fig. 1. Cyclic voltammetric behavior of 2 Ω carbon resistor electrode in electrolyte, scan rate 100 mV s^{-1}. a) 1.0 M $HClO_4$, third cycle b) pH 4.6 0.1 M acetate buffer, after three cycles in 1.0 M $HClO_4$.

3. Results and Discussion

The electrochemical behavior of the thin film carbon electrodes has been tested through a number of different experiments, the most relevant of which will be discussed below. Where appropriate comparison will be made with previous studies on glassy carbon electrodes pyrolyzed at different temperatures [18] and with other types of carbon electrode.

3.1. Potential Window

The most important criterion for a good performance is a wide useable potential window. To investigate this range, potential scans were first carried out in sodium acetate buffer electrolyte with poor and irreproducible results. Following this, it was decided to use electrochemical pretreatment by cycling the electrodes in perchloric acid, similar to the treatment carried out in [6], the maximum oxidation and reduction currents being limited to 1 mA. Under these conditions, oxidation and reduction peaks were observed, see Figure 1a, a relatively stable response being obtained after 3 cycles. Further cycling did not lead to any alteration in response, and this was checked with a number of electrodes. On returning to acetate buffer electrolyte, Figure 1b, an excellent potential window was observed with little hysteresis. Thus this pretreatment method was used in all subsequent experiments. The different negative potential limits seen in Figure 1a and b can be ascribed principally to the influence of pH on the potential of the hydrogen evolution reaction. Potentials at which the current reached 100 µA cm^{-2} at this scan rate of 100 mV s^{-1} were approximately $+1.6$ V and -1.5 V.

This sequence of scans was repeated for different carbon film electrodes, with good reproducibility after pretreatment. A second example is shown in Figure 2, where the background currents for the voltammograms in perchloric acid during pretreatment are significantly poorer than those obtained for the resistor in Figure 1, and the oxidation and reduction peaks are more pronounced. Nevertheless, after pretreatment the background currents are even lower than those shown in Figure 1b.

The nature of the oxidation and reduction peaks on glassy carbon has been discussed in the literature in terms of oxidation and reduction of a graphitic oxide film on the surface [18, 19]. Since the peaks observed in this article, (see Fig. 1), occur at the same values of potential as in [18] and [19], a similar explanation can be invoked. Removal of oxygen from solution reduced the size of the peaks but, if at least 5 cycles were done during pretreatment, made no noticeable difference to the final cyclic voltammetric behavior.

Comparing the potential window with that of the glassy carbon studied in [18], following pyrolysis at 2500 °C – necessary to give the cleanest electrochemical behavior – the potential window within which the current remained less than 100 µA cm^{-2} was -1.2 to $+1.2$ V (vs. SCE) in 0.5 M H_2SO_4 solution and was -1.5 to $+1.5$ V in 0.4 M K_2SO_4 solution.

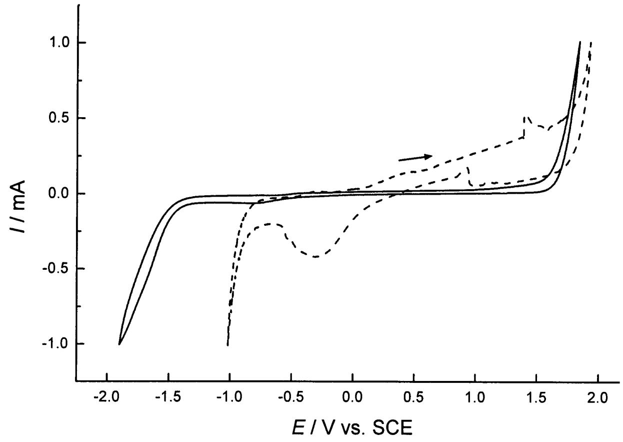

Fig. 2. Cyclic voltammograms at a different carbon resistor electrode: (⋯ ⋯) 1.0 M $HClO_4$, third cycle, (——) pH 4.6 0.1 M acetate buffer, after three cycles in 1.0 M $HClO_4$.

Further comparison was made with Tokai GC 20 glassy carbon electrodes, as shown in Figure 3. In this case, the background current in highly acidic solution is better than at the carbon films. However, in acetate buffer solution, the potential window is similar and the background currents are larger than at the carbon films. This has important consequences for reactions that need to be studied close to these limits.

Differences between diamond films and these carbon films can be ascribed to the surface microstructure. Diamond films are made by pyrolysis of dilute mixtures of a hydrocarbon gas, such as methane, in hydrogen using energy-assisted chemical vapor deposition – hot-filament or microwave discharge which leads to a sp^3-hybridized structure and less interaction with species in solution. The carbon film resistors used unreactive nitrogen as the main gas with heating which precludes the formation of methyl radicals and atomic hydrogen and leads to a more reactive sp^2-hybridized graphite microstructure [20, 21].

Although an exact comparison of the experimental conditions is not possible, these carbon film resistor electrodes appear to have a potential window at least as large and often larger than glassy carbon using the electrochemical pretreatment described. Background currents are low, as shown in Figures 1 and 2. The calculated values of capacitance from impedance spectra were around 30 $\mu F\,cm^{-2}$, similar to glassy carbon and larger than that of highly oriented pyrolytic graphite [22].

3.2. Oxidation of Potassium Hexacyanoferrate(II)

Standard electroactive species have been used to test the behavior of the carbon film resistor electrodes. For carbon electrodes there are much data in the literature concerning the oxidation of hexacyanoferrate(II), particularly regarding the electrode kinetics of this reaction, which is strongly dependent on the state of and species on the electrode surface [2, 18]. There are also important ageing effects, which can influence the measured currents, often due to surface blocking, and also the electrode kinetics owing to alterations of the surface groups on the carbon. The pretreatment can be particularly influential on the response.

Figure 4 illustrates results obtained for the oxidation of hexacyanoferrate(II) using cyclic voltammetry at a number of different scan rates. These voltammograms were obtained directly after electrochemical pretreatment in perchloric acid and no alterations were observed with time on repeated cycling or after several hours. This is in contrast to most glassy carbons [2]. There is a slight increased peak separation on increasing scan rate. Peak currents follow a linear relationship with the square root of the scan rate, as predicted for hexacyanoferrate(II), and the ratio of peak currents is close to one. However, at high scan rates the noise level increases, presumably owing to the non-uniformities in the electrode surface morphology.

Estimations were made of the standard rate constant, k_0, using software fitting of the cyclic voltammetric curve, assuming that the diffusion coefficients of hexacyanoferrate(II) and hexacyanoferrate(III) are the same and equal to $0.62 \times 10^{-5}\,cm\,s^{-1}$ [16]. This led to calculated values of k_0 between 6 and $8 \times 10^{-3}\,cm\,s^{-1}$, and a half-wave potentials constant at $+0.223$ V (vs. SCE). Such results compare favorably with values obtained for glassy carbon under similar experimental conditions [18]. In [18], values between 9 and $11 \times 10^{-3}\,cm\,s^{-1}$ were found for glassy carbon heat-treated at 2500 °C.

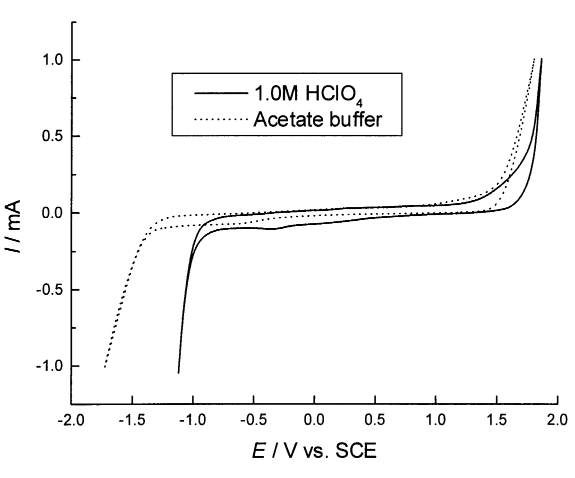

Fig. 3. Cyclic voltammetry at Tokai GC20 glassy carbon: (——) 1.0 M $HClO_4$, third cycle, (⋯⋯) pH 4.6 0.1 M acetate buffer, after three cycles in 1.0 M $HClO_4$.

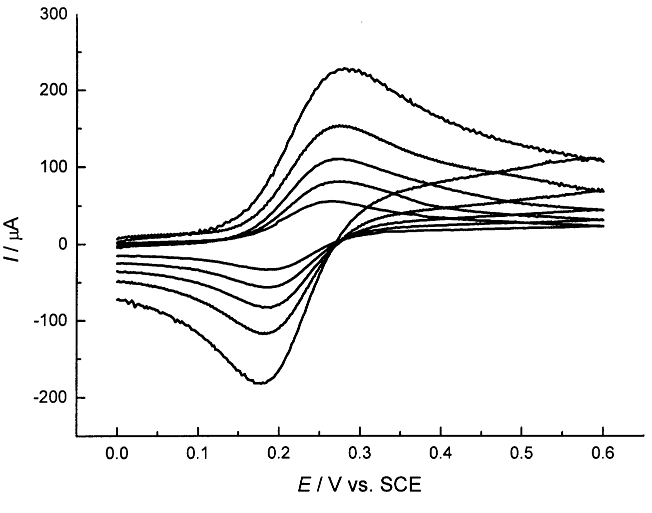

Fig. 4. Cyclic voltammograms after background subtraction for oxidation of 1 mM $K_4Fe(CN)_6$ in 0.4 M K_2SO_4 electrolyte at scan rates of 20, 50, 100, 200 and 500 $mV\,s^{-1}$.

These results suggest that, following the electrochemical activation described above, these carbon film electrodes can be used in the potential range close to 0 V as a direct substitute for other types of carbon electrode and apparently with fewer problems of alterations with time of immersion in the electrolyte solution. It is now of interest to extend their possibilities to the limits of the potential window.

3.3. Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) of heavy metal ions is still often carried out at liquid mercury or mercury film electrodes as discussed above. In many applications, mercury films are formed on glassy carbon substrates since this electrode material can also be conveniently used in the positive potential range. There is a tendency to form a collection of contacting droplets instead of a uniform film, and conditions for mercury film formation must be carefully chosen to avoid any influence from droplet formation. Additionally, physical migration of the mercury over highly polished glassy carbon surfaces can occur if care is not taken, particularly when there is convective flow of the solution. These and other aspects have been discussed in the literature [23]. Other electrode substrates can form "amalgam-films" and are thus not so versatile over the full potential range [24], although iridium is a good candidate for film formation without amalgamation. Nevertheless, electrode preparation takes time and thus, in addition to environmental considerations, there is necessity for an electrode material that can be used directly for oxidation and reduction studies. Various approaches to solve the mercury problem have been suggested, as described in the introduction.

The carbon film electrodes investigated in this article have therefore been evaluated, after the 3-cycle electrochemical activation procedure in perchloric acid, as a direct substitute for mercury film electrodes, which would confer a number of practical advantages. Results are shown concerning the analysis of trace zinc ions, given that in most electroanalytical procedures zinc ions need to be reduced at potentials of at least -1.5 V (vs. SCE). This therefore represents a more difficult application than the lead ions described in [16], and can be compared with the measurement of a mixture of zinc, cadmium and lead ions described in [17]; both of these procedures were carried out at diamond film electrodes. The ASV of zinc ions at mercury film-coated glassy carbon electrodes is well documented [25, 26]: a positive-going square-wave voltammetric scan leads to a zinc reoxidation peak appearing between -1.2 V and -1.0 V (vs. SCE), according to the electrolyte employed.

A typical series of traces obtained for square-wave anodic stripping voltammetry of zinc ions without solution deoxygenation is shown in Figure 5. The peak is well-defined despite the high background current below -1.4 V (vs. SCE). Peak half-width, $W_{1/2}$, is ca. 58 mV in all cases and peaks are close to symmetrical.

Theory for anodic stripping square-wave stripping voltammetry at mercury film electrodes for film thickness tending to zero can be directly applied. This situation corresponds to no diffusion restrictions within the mercury film and is thus analogous to a solid deposit on the electrode. It was shown in [27] for very thin films, that $nW_{1/2} = 99$ mV, which corresponds to 49.5 mV for a two-electron oxidation. This suggests that there are some kinetic effects in SWASV at the carbon film, which may reflect the time needed for the electrodeposit to be removed from the surface of the electrode.

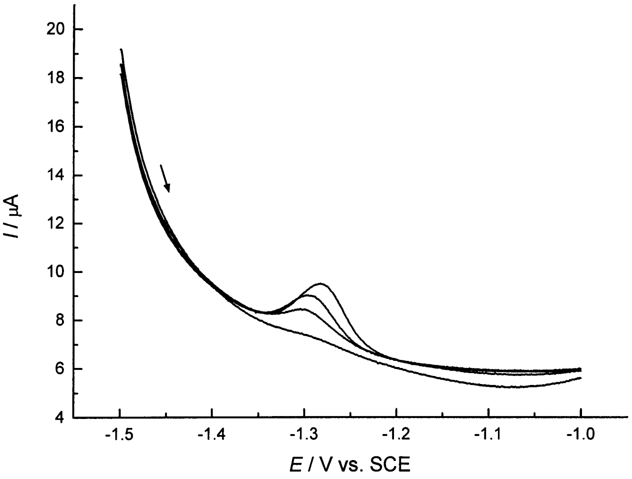

Fig. 5. Square-wave anodic stripping voltammetry of zinc ions in 0.1 M $NaClO_4$ electrolyte. Each trace represents addition of 0.1 μM Zn^{2+} to blank electrolyte. $E_{dep} = -1.55$ V, $t_{dep} = 120$ s. Square-wave scan initiated at -1.50 V, parameters $f = 25$ Hz, scan increment 1 mV, amplitude 20 mV.

Analysis of the results obtained in these experiments with 120 s deposition gives the following equation for the calibration curve: $I(\mu A) = 0.051 + 0.072c$ ($n = 6$), where c is $[Zn^{2+}]$ measured in $\mu mol\,dm^{-3}$. The detection limit (based on 3σ) is $7\,nmol\,dm^{-3}$. Lower limits can be expected with longer deposition times. In the preliminary study in [17] at diamond films, the detection limit attained was described as "low ppb" – $1\,\mu mol\,dm^{-3}$ corresponds to $15\,nmol\,dm^{-3}$ – so that the results obtained here show a worthwhile improvement.

Finally, Figure 6 shows an experimental SWASV trace of zinc plus cadmium and lead ions at the carbon film electrode and demonstrates that the three ions can easily be determined simultaneously with good peak separation.

Further work is being carried out to examine the details of the anodic stripping voltammetry process and the use of these electrodes as inexpensive ASV sensors.

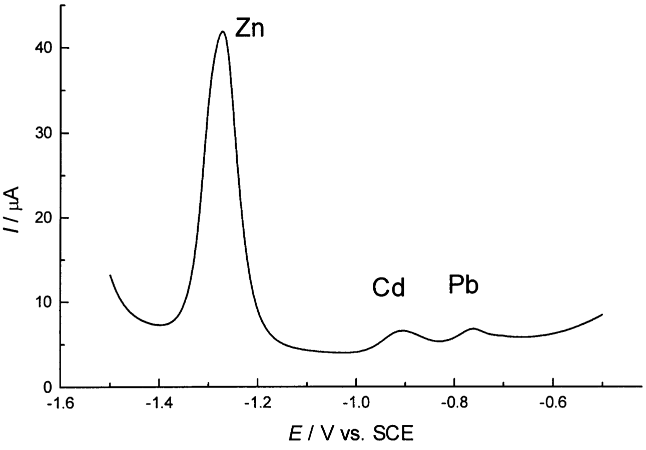

Fig. 6. Square-wave anodic stripping voltammetry of zinc, cadmium and lead ions $[Zn^{2+}] = 10^{-6}\,mol\,dm^{-3}$, $[Cd^{2+}] = [Pb^{2+}] = 10^{-7}\,mol\,dm^{-3}$ in 0.1 M $NaClO_4$ electrolyte. Other experimental conditions as in Figure 5.

4. Conclusions

It has been shown that carbon film resistors show promise as a new electrode material in both the positive and negative potential range in aqueous solution with a wide available potential window. The possibility of their use in stripping voltammetry is of particular importance for replacing mercury electrodes, with their associated well-known environmental problems.

Changes in the fabrication procedure to make more robust carbon films may lead to increased reproducibility and ability to further widen the potential range without compromising film integrity. The low price of carbon resistors means that their use is very attractive.

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6. References

[1] C.M.A. Brett, *Electroanalysis* **1999**, *11*, 1013.
[2] R.L. McCreery, in *Electroanalytical Chemistry*, Vol. 17 (Ed: A.J. Bard), Marcel Dekker, New York **1991**, pp. 221–374.
[3] N.L. Pocard, D.C. Alsmeyer, R.L. McCreery, T.X. Neenan, M.R. Callstrom, *J. Mater. Chem.* **1992**, *2*, 771.
[4] J.W. Strojek, M.C. Granger, G.M. Swain, T. Dallas, M.W. Holtz, *Anal. Chem.* **1996**, *68*, 2031.
[5] J. Xu, M.C. Granger, Q. Chen, J.W. Strojek, T.E. Lister, G.M. Swain, *Anal. Chem.* **1997**, *69*, 591A.
[6] K. Yoo, B. Miller, R. Kalish, X. Shi, *Electrochem. Solid-State Lett.* **1999**, *2*, 233.
[7] A. Rojo, A. Rosenstratten, D. Anjo, *Anal. Chem.* **1986**, *58*, 2988.
[8] D.M. Anjo, S. Brown, L. Wang, *Anal. Chem.* **1993**, *65*, 317.
[9] O. Niwa, T. Horiuchi, H. Tabei, *J. Electroanal. Chem.* **1994**, *367*, 265.
[10] Kh.Z. Brainina, E. Neyman, *Electroanalytical Stripping Methods*, Wiley, New York **1993**.
[11] C.M.A. Brett, A.M.C.F. Oliveira Brett, *J. Electroanal. Chem.* **1989**, *262*, 83.
[12] Kh.Z. Brainina, *Anal. Chim. Acta* **1995**, *305*, 146.
[13] Kh.Z. Brainina, A.M. Bond, *Anal. Chem.* **1995**, *67*, 2586.
[14] Kh.Z. Brainina, A.V. Ivanova, N.A. Malakhova, *Anal. Chim. Acta* **1997**, *349*, 85.
[15] Kh.Z. Brainina, N.A. Malakhova, A.V. Ivanova, in *Biosensors for Direct Monitoring of Environmental Pollutants in the Field* (Eds: D.P. Nikolelis, U.J. Krull, J. Wang, M. Mascini), Kluwer, Dordrecht **1998**, pp. 255–269.
[16] A. Manivannan, D.A. Tryk, A. Fujishima, *Electrochem. Solid State Lett.* **1999**, *2*, 455.
[17] M.C. Granger, J. Xu, J.W. Strojek, G.M. Swain, *Anal. Chim. Acta* **1999**, *397*, 145.
[18] H. Maleki, C.J. Cojocaru, C.M.A. Brett, G.M. Jenkins, J.R. Selman, *J. Electrochem. Soc.* **1998**, *145*, 721.
[19] A.L. Beilby, T.A. Sasaki, H.M. Stern, *Anal. Chem.* **1995**, *67*, 976.
[20] A. Argoitia, J.C. Angus, J.S. Ma, L. Wang, P. Pirouz, W.R.L. Lambert, *J. Mater. Res.* **1994**, *9*, 1849.
[21] H.B. Martin, A. Argoitia, J.C. Angus, U. Landau, *J. Electrochem. Soc.* **1999**, *146*, 2959.
[22] G.M. Swain, T. Kuwana, *Anal. Chem.* **1992**, *64*, 565.
[23] W. Frenzel, *Anal. Chim. Acta* **1993**, *273*, 123.
[24] S.P. Kounaves, J. Buffle, *J. Electroanal. Chem.* **1987**, *216*, 53.
[25] C.M.A. Brett, M.M.P.M. Neto, *J. Chem. Soc., Faraday Trans. I* **1986**, *82*, 1071.
[26] C.M.A. Brett, A.M. Oliveira Brett, L. Tugulea, *Anal. Chim. Acta* **1996**, *322*, 151.
[27] S.P. Kounaves, J.J. O'Dea, P. Chadresekhar, J. Osteryoung, *Anal. Chem.* **1987**, *59*, 386.