Silicon carbide: a new electrode material for voltammetric measurements

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Chemical vapour deposition of tetramethylsilicon at a resistively heated carbon fibre substrate produces a concentric silicon carbide conductor suitable for use as a solid electrode material for electrochemical measurements.

Silicon carbide (SiC) is a hard, chemically inert, wide bandgap semiconductor ceramic material.[1] However, when appropriately doped with hydrogen, the conductivity of SiC dramatically increases and exhibits electrical characteristics not unlike carbon materials.[2] The utility of carbon materials as solid electrodes for electrochemical measurements is well documented as is the variability of the electron-transfer characteristics between different carbon forms and surfaces.[3,4] Although a better understanding of the relationship between surface structure and electron-transfer kinetics is emerging for carbon,[5] the lack of a well defined regular surface can lead to poor reproducibility in electrochemical measurements. In contrast to carbon, SiC has either a closest packed hexagonal (α-SiC) or cubic (β-SiC) structure which should afford a well defined surface for electron transfer.[1] Thus, it is surprising that doped SiC has not been utilized as an electrode material for electrochemistry.

Recently, we have developed a novel chemical vapour deposition (CVD) method for the modification and fabrication of ultramicroelectrode[6–8] and optically transparent electrode[9] devices. This approach is based on the deposition of micrometre thick films of conducting or insulating materials onto conducting substrates. Film formation occurs as a result of decomposition of molecular gas-phase precursor systems at the surface of resistively heated electrode substrates. In this report, CVD technology is used to produce films of millimetre dimensions for the purpose of investigating new materials as potential solid electrodes for voltammetric measurements. As an alternative to carbon as a solid electrode for voltammetric analysis, we describe herein the pyrolysis of tetramethylsilicon ($SiMe_4$, TMS) to yield conducting electrodes of silicon carbide.[10] Preliminary electrochemical results at this promising solid electrode material are also presented.

Silicon carbide electrodes were prepared by modification of the previous CVD method for coating carbon fibres.[8] A 10 μm carbon fibre was used as the substrate upon which SiC was deposited by the following procedure. The carbon fibre was resistively heated in an argon atmosphere to temperatures between 750 and 1180 °C. TMS (10 ml h^{-1}) in a stream of argon (300 ml min^{-1}) was then passed over the hot surface, which resulted in the decomposition of TMS and deposition of a coating of SiC on the carbon substrate. Inclusion of 5% H_2 in the argon stream had no noticeable effect on the deposition process. In this temperature range, coatings were obtained with growth rates from 10 to 200 μm h^{-1} depending on the TMS concentration and the substrate temperature. In a typical procedure, concentric coatings were obtained between 840 and 940 °C with growth rates of approximately 50 μm h^{-1}. Coated fibres with diameters up to 1.4 mm were obtained by this procedure.

A typical SEM micrograph of an unpolished SiC coated carbon fibre is shown in Fig. 1. The coating is concentric about the carbon fibre with a total diameter of approximately 0.40 mm. Magnification of the coated fibre in Fig. 1 reveals no visible gaps at the carbon fibre and SiC coating interface, which indicates good adhesion of the coating to the fibre was obtained. Qualitative characterization of the coating with SEM/EDX shows the presence of only silicon and carbon with hydrogen being spectroscopically absent during EDX analysis. Hydrogen incorporation into the coating is confirmed by the electrochemical measurements, *vide infra*.

Electrodes for electrochemical measurements were prepared by removing the coated fibre from the fibre holder, cutting it into two equal sections of 5–6 mm with a fibre optics cleaver, and attaching a copper lead to one end with conducting silver epoxy. The coated fibres were then embedded in an insulating epoxy and were sequentially polished with 10 μm alumina and 6 μm diamond polishing slurries. Finally, the electrodes were sonicated before use. Electrode surface areas were measured by chronoamperometry of a standard 75 μM ferrocyanide solution in 1 M KNO_3 ($D_o = 6.1 \times 10^{-6}$ cm^2 s^{-1} at 24 °C).[11] For the electrode in Fig. 1, the geometric surface area from SEM micrographs was found to be $1.71 \pm 0.15 \times 10^{-3}$ cm^2, while the electrochemically determined surface area was $1.81 \pm 0.19 \times 10^{-3}$ cm^2. The agreement between the SEM and the electrochemical results confirms the electroactivity of the deposited SiC coating and that good adhesion of the coating to the carbon fibre is obtained.

Cyclic voltammetry at the SiC electrode in a 0.1 M H_2SO_4 solution demonstrated a wide potential window free from interferences from +1.4 to −1.2 V *vs.* Ag/AgCl for performing voltammetric measurements. Importantly, the hydrogen overpotential in the negative potential region is comparable to the glassy carbon electrode. Fig. 2 demonstrates the electrochemical response of an aqueous solution of 5 mM methyl viologen (MV^{2+}) with 50 mM NaCl at the SiC electrode. The characteristic sequential one-electron reductions for MV^{2+} to MV at a macroscopic solid electrode are readily observed in this potential range at $E_{pc} = -0.70$ and -0.97 mV *vs.* Ag/AgCl. The redox behaviour of MV^{2+} is similar to that reported by Kaifer and Bard[12] in 50 mM NaCl except that adsorption of MV is not observed under these conditions at the SiC electrode. It may be reasonable that the diminished adsorption at the SiC

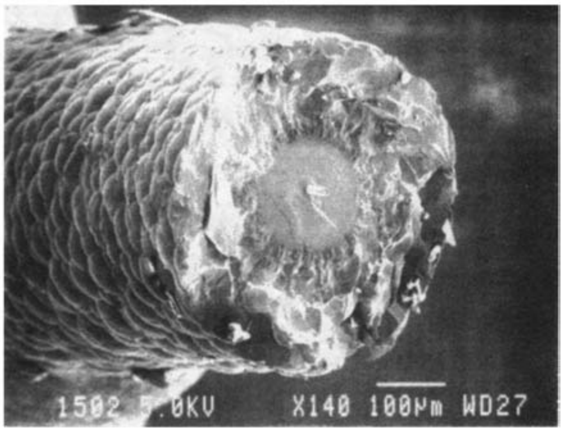

Fig. 1 Scanning electron micrograph of an unpolished SiC coated carbon fibre; magnification (140×) and working distance (27 mm)

electrode is in part due to the difference in surface structure of SiC relative to glassy carbon.

Chemical vapour deposition shows promise as a route for the preparation of new solid electrode materials. Preliminary results indicate the SiC electrode exhibits similar electrochemical characteristics to carbon and warrants further study as a solid electrode material. Further characterization of the SiC electrode and other solid electrode materials is in progress.

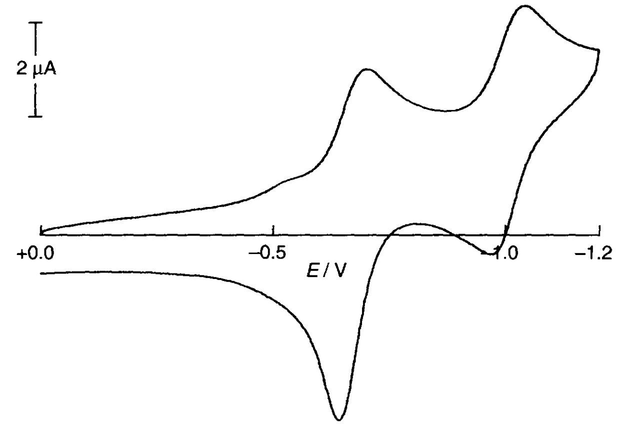

Fig. 2 Cyclic voltammogram of an aqueous solution of 5 mM methyl viologen with 50 mM NaCl at a polished SiC electrode; scan rate = 100 mV s^{-1}, electrode diameter = 1.4 mm

The University of Toledo and the College of Arts and Sciences are gratefully acknowledged for support of the scanning electron microscope facility.

References

1 *Silicon Carbide: A High Temperature Semiconductor, Proceedings on Silicon Carbide,* ed. J. R. O'Connor and J. Smittens, Pergamon Press, Boston, 1960; H. O. Pierson, *Handbook of Chemical Vapor Deposition (CVD): Principles, Technology and Applications*, Noyes Publication, Park Ridge, NJ, 1992, p. 208.
2 V. Chu, J. P. Conde, J. Jarego, P. Brogueira, J. Rodriguez, N. Barradas and J. C. Soares, *J. Appl. Phys.*, 1995, **78**, 3164.
3 K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, New York, 1988.
4 R. L. McCreery, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1991, vol. 17, pp. 221–374.
5 R. L. McCreery and K. K. Cline, in *Laboratory Techniques in Electroanalytical Chemistry*, ed. P. T. Kissinger and W. R. Heineman, Marcel Dekker, New York, 1996, ch. 10.
6 G. Zhao, D. M. Giolando and J. R. Kirchhoff, *J. Electroanal. Chem.*, 1994, **379**, 505.
7 G. Zhao, D. M. Giolando and J. R. Kirchhoff, *Anal. Chem.*, 1995, **67**, 1491.
8 G. Zhao, D. M. Giolando and J. R. Kirchhoff, *Anal. Chem.*, 1995, **67**, 2592.
9 M. Kummer and J. R. Kirchhoff, *Anal. Chem.*, 1993, **65**, 3720.
10 J. Fölsch, H. Rübel and H. Schade, *J. Appl. Phys.*, 1993, **73**, 8485.
11 R. V. Bucur, A. Bartes and V. Mecea, *Electrochim. Acta*, 1978, **23**, 641.
12 A. E. Kaifer and A. J. Bard, *J. Phys. Chem.*, 1985, **89**, 4876.

Received, 12th July 1996; Com. 6/04901J