

Electrochemical studies of kerosene-pyrolysed carbon films

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Polycrystalline thin films of conducting carbon are deposited on alumina substrates by the pyrolysis of kerosene vapour at 1000 °C for 2 h in argon atmosphere. Preliminary structural analysis is done by XRD, laser-Raman, FTIR and SEM studies. The electrochemical behaviour of as-grown conducting carbon films was investigated in various electrolytes at different pH and the performance was compared with that of platinum and glassy electrodes. The electrochemical window of the kerosene carbon electrode in 100 mM H₂SO₄ was found to be 2.91 V which is greater than that of glassy carbon (2.79 V) and platinum (2.02 V). Cyclic voltammetry reveals that Pt electrode has almost an equal tendency towards hydrogen and oxygen evolution, whereas glassy carbon favours hydrogen evolution and kerosene carbon favours oxygen evolution. It is suggested that the kerosene carbon electrode can be used as an oxygen electrode more efficiently. Unlike diamond films or glassy electrodes, kerosene carbon thin films are of low cost and good stability; they are also easy to grow on various ceramic substrates of any size. Moreover, these electrodes are very economical and promising for application in chlor-alkali industry.

Keywords: *conducting carbon, electrochemical, kerosene, thin film*

1. Introduction

In electrochemical studies, commonly used inert electrodes are platinum, carbon paste, graphite, glassy carbon. Although platinum is the most common electrode, its metallic shiny surface makes electron transfer difficult, unless the electrode is in the platinized black form. Graphite electrodes, although inert, produce carbon dust in the electrolyte if used continuously for a long period. Glassy electrodes, on the other hand, are preferred due to their greater inertness and stability in solution. The cost of glassy electrodes and the limitation of the size available commercially, limits their use to the laboratory scale only. Recently, the growth of synthetic boron-doped polycrystalline diamond films and diamond-like carbon (DLC) films from the cracking of methane under various laboratory conditions have made it possible to study the application of such films in electrochemical work, especially because polycrystalline diamond films or DLC films can be made conducting and are expected to be chemically/electrochemically stable in aqueous solution [1–5]. However, these electrodes are still in the early stages of development and their method of preparation limits their commercialisation for large scale applications. Elec-

trochemists are, therefore, searching materials for making large sized electrodes which are economical, noncorrosive, chemically and electrochemically inert, and which possess a larger electrochemical potential window than that of glassy carbon or platinum electrodes in aqueous solutions.

The electrochemical stability of polycrystalline diamond films or DLC films is higher than that of graphite due to the incorporation of sp³ carbon atoms into the matrix of sp² carbon atoms in DLC films. Polycrystalline diamond or DLC films have been synthesized by chemical vapour deposition (CVD) of methane gas in the presence of hydrogen [6]. The presence of 100% sp³ carbon atoms in a polycrystalline diamond film makes it an insulator unless heavily doped with boron or phosphorous. Inclusion of a few sp² carbons in a DLC film, causes it to become a conductor. But CVD or other conventional methods for the synthesis of DLC or polycrystalline diamond films demand very stringent conditions. Moreover, it is difficult to prepare large sized films by these methods. Therefore, a simpler technique and cheaper carbon precursors are needed for the synthesis of conducting carbon films having properties similar to that of DLC or glassy carbon and yet easy to grow in large sizes for industrial application.

Recently, Sharon *et al.* reported the formation of polycrystalline diamond, DLC as well as glassy

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carbon films by simple pyrolysis of a natural precursor, camphor [7–10]. Following a similar technique, we have obtained conducting carbon thin films from a cheap petroleum product, kerosene. The basic advantage of this technique and the precursor is that conducting carbon thin films can be deposited on any ceramic substrate by mere pyrolysis of kerosene vapour at a suitable temperature, without using a catalyst or hydrogen gas. Unlike the conventional methods of preparation of polycrystalline diamond film or DLC film, the pyrolysis of camphor or kerosene does not require doping of the film, because it readily yields a highly conducting carbon film. The method is simple, economical and forms highly adherent films (thickness 1–100 μm) on a variety of ceramic substrates of any shape and size. In this paper we report the electrochemical behaviour of polycrystalline conducting carbon films grown by the pyrolysis of kerosene vapour on alumina plates; this is followed by their application in the electrolysis of brine solution.

2. Experimental details

Thin films of carbon were deposited on alumina substrates by the pyrolysis of kerosene vapour at 1000 °C for 2 h in argon atmosphere [7]. No pre- or post-treatments were done in this deposition. The polycrystalline structure of as-grown carbon film was investigated by XRD analysis with a Philips X-ray diffractometer (model 1806) using CuK_α radiation. The unit cell size was ascertained by a computer programmed X-ray analysis software. Surface morphology was studied by SEM analysis by a Cameca scanning electron microscope (model SU30). The laser-Raman spectrum was taken on a Ramanor HG2S and Fourier transform infrared (FTIR) spectra were analysed by an IR spectrophotometer (model Impact 400) of the Nicolet Instruments Corporation.

For the electrochemical study of as-grown conducting carbon films, a three-electrode single compartment electrochemical cell containing a large area counter electrode of platinum and a reference electrode of saturated calomel was used. Cyclic voltammetric investigations were carried out in (i) 100 mM H_2SO_4 , (ii) 100 mM NaOH , (iii) 100 mM $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ + 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ (at pH 4 and 9.20) and (iv) 100 mM $(\text{NH}_4)_2(\text{FeSO}_4)_2 \cdot 6\text{H}_2\text{O}$ + 100 mM $\text{NH}_4(\text{FeSO}_4)_2 \cdot 12\text{H}_2\text{O}$ (pH 3) electrolytes, successively. The cyclic voltammograms were recorded by a computer programmed interface device using a EG&G PAR model Versastat. To compare the results, these experiments were also repeated with glassy carbon and platinum electrodes. The effect of scan rate on the anodic and cathodic current was also studied. In another set of experiments, the electrolysis of 30% brine solution was carried out with kerosene carbon electrodes for a long period at various current densities.

3. Results and discussion

3.1. Structural analyses

Figure 1 shows an XRD pattern of kerosene-pyrolysed carbon film which reveals one weak peak at 16.94° and one strong, broad peak at $2\theta = 25.84^\circ$. As-obtained d -values were found to fit into a hexagonal lattice arrangement with the unit cell size $a = b = 701.25$ pm and $c = 2008.75$ pm with c/a ratio 2.86. Though these values are not in good agreement with those of graphitic carbon as per the ASTM powder diffraction file [11], the c/a ratio for the kerosene carbon lies within the reported range of c/a values for graphites [12–14]. This suggests that the kerosene-pyrolysed carbon structure is close to that of graphite. Since glassy carbon and graphite have very similar XRD patterns, the laser-Raman spectrum of the film was taken for verification. However, it was surprising that no peak appeared in the vicinity of 1357 and 1583 cm^{-1} (responsible for glassy carbon) or 1580 cm^{-1} (responsible for graphite); suggesting that the kerosene-pyrolysed carbon is neither graphitic nor glassy carbon.

The room temperature electrical resistivity of as-grown film was found to be $1.4 \times 10^{-4}\ \Omega\text{ cm}$. The carrier concentration and Hall mobility were found to be $6.354 \times 10^{14}\text{ cm}^{-3}$ and $6.97 \times 10^7\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively. Hall measurements suggest the kerosene carbon to be n-type. The sp^2 and sp^3 carbon contents in the film were found in a ratio of 17 : 5, as calculated from the FTIR spectrum (not shown here). The presence of sp^3 carbon may be a reason for the deviation of kerosene-pyrolysed carbon structure from the graphitic structure. A smaller c/a ratio (2.86), as compared to 8.2 reported for graphite [13], may also be due to the presence of sp^3 carbon in the kerosene carbon.

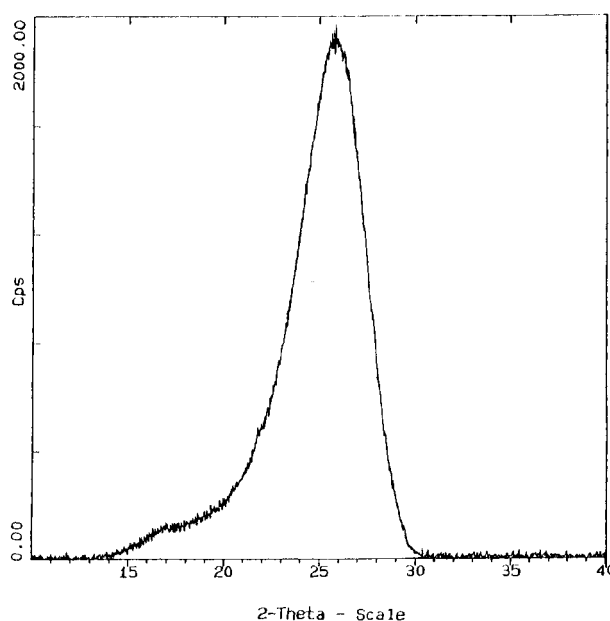


Fig. 1. X-ray diffraction pattern for the kerosene-pyrolysed carbon film.

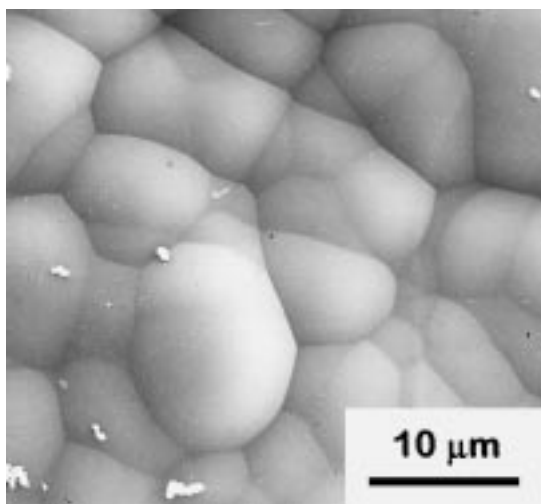


Fig. 2. Scanning electron micrograph of the kerosene-pyrolysed carbon film.

Figure 2 exhibits the scanning electron micrograph of the kerosene-pyrolysed carbon film. Well defined grain boundaries are indicated. The grain size, however, varies from 5–15 μm . The film has a good adherence to the alumina substrate as examined by the Scotch tape test.

3.2. Electrochemical analyses

The electrochemical potential window of kerosene-pyrolysed carbon film in contact with H_2SO_4 and NaOH solutions was investigated in a potential range 2.5 to -1.5 V vs SCE at different scan rates. The same experiment was repeated with platinum and glassy carbon electrodes using a Pt counter electrode. The exposed area of all the working electrodes was kept constant (0.12 cm^2) in each experiment, for the sake of direct comparison of their I/V plots. As-obtained cyclic voltammograms (CVs) in $100\text{ mM H}_2\text{SO}_4$ solution are shown in Fig. 3(a)–(d). The anodic and cathodic potentials corresponding to oxygen and hydrogen evolution, respectively. As seen from the Fig. 3(a)–(c), the kerosene carbon has the widest potential window (2.91 V) as compared to Pt (2.02 V) and glassy carbon (2.79 V). Careful observation of these experiments suggests that the kerosene carbon electrode can be used as an oxygen electrode more efficiently, whereas glassy electrode is preferred as a hydrogen electrode. Platinum electrode, however, shows almost an equal tendency towards hydrogen and oxygen evolutions. Figure 3(d) shows the performance of the kerosene carbon as a counter electrode. Comparison of Fig. 3(d) with 3(c) suggests that the kerosene carbon electrode is as good as a platinum counter electrode. The electrochemical windows obtained with these electrodes are given in Table 1. The background current with the kerosene carbon, glassy carbon and platinum electrodes were registered in the vicinity of 60, 40 and $30\ \mu\text{A cm}^{-2}$, respectively.

Figure 4 shows the CVs of the kerosene carbon and Pt electrodes (both with Pt counter) in 100 mM

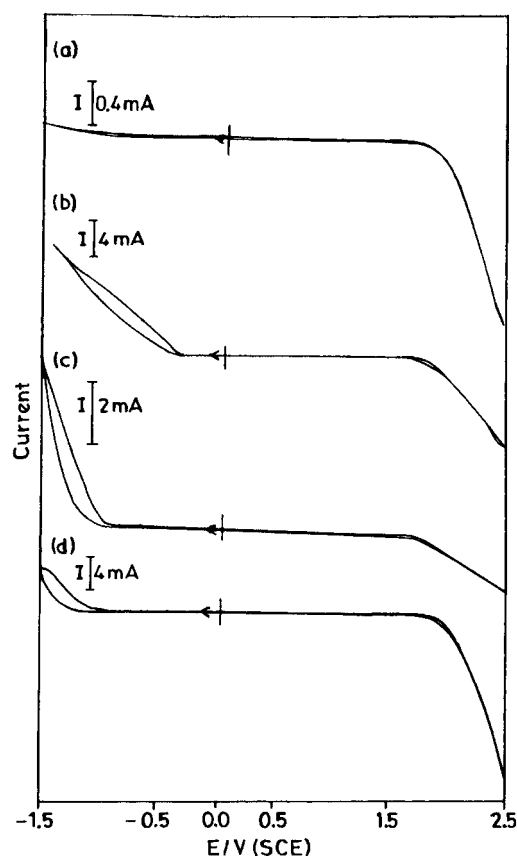


Fig. 3. Cyclic voltammograms of: (a) kerosene carbon with Pt counter; (b) Pt electrode with Pt counter; (c) glassy carbon with Pt counter; (d) glassy carbon with kerosene carbon counter. All working electrodes have equal geometrical area (0.12 cm^2) exposed to the electrolyte ($100\text{ mM H}_2\text{SO}_4$) and the CVs are taken at a scan rate of 20 mV s^{-1} .

NaOH solution at a scan rate 100 mV s^{-1} . A larger potential window for the kerosene carbon (as compared to Pt) is also evidenced in alkaline medium. Moreover, comparison of Fig. 4 with Fig. 3(a) reveals that, though the potential windows of the kerosene carbon in acidic and alkaline media are of the same magnitude, there is a negative shift of 180 mV in the CV in alkaline medium. Also a deviation in the hydrogen evolution onset potential is observed in the cathodic and anodic scans.

The CV of the kerosene carbon (Fig. 3(a)) is in contrast to that of the single crystal semiconducting CVD diamond electrode in 1 M KOH and

Table 1. Electrochemical potential windows of various inert electrodes as observed in $100\text{ mM H}_2\text{SO}_4$ solution

Electrodes		Hydrogen evolution vs SCE/V	Oxygen evolution vs SCE/V	Window/V
Working	Counter			
Kerosene carbon	Pt	-1.24	1.67	2.91
Platinum	Pt	-0.38	1.64	2.02
Glassy carbon	Pt	-1.07	1.72	2.79
Glassy carbon	kerosene carbon	-1.00	1.75	2.75

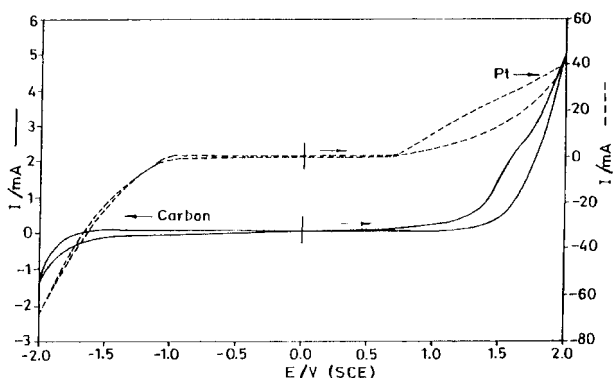


Fig. 4. CV of kerosene carbon with Pt counter (—) and Pt electrode with Pt counter (---) in 100 mM NaOH solution at a scan rate 100 mV s^{-1} .

$0.5 \text{ M H}_2\text{SO}_4$, as reported by Lagemaat *et al.* [5]. They observed almost rectifying behaviour in the cathodic mode up to -1 V vs Ag/AgCl, but in the anodic scan, oxygen evolution was noticed around 1.5 V . Swain *et al.* [3] have reported a similar behaviour with boron-doped diamond films grown by CVD. However, they found a narrow electrochemical potential window for this material. As a matter of fact, the electrochemical window of polycrystalline diamond depends on the degree of purification of the electrode. Martin *et al.* [6] have found a fairly large electrochemical potential window of 3.5 V for electrochemically treated polycrystalline diamond film deposited on a tungsten wire of diameter 0.05 cm . In the present work the kerosene-pyrolysed carbon films yielding the electrochemical window of 2.91 V were deposited on alumina substrates of dimension $1 \text{ cm} \times 1 \text{ cm}$. Whether the polycrystalline diamond electrode of size 1 cm^2 would possess the same window as that shown by the small area film [6] remains to be examined.

The electrochemical behaviour of the kerosene carbon was studied in commonly used redox electrolytes at different pH using cyclic voltammetry at different scan rates. Typical CVs for (a) Kerosene carbon working electrode with Pt counter and (b) Pt working electrode with Pt counter; as observed in $100 \text{ mM K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{ H}_2\text{O} + 10 \text{ mM K}_3\text{Fe}(\text{CN})_6$ (pH 9.2, buffer) are shown in Fig. 5. The scan was started from 0 V (SCE) in the anodic direction. The scan rate was 50 mV s^{-1} . As seen from the Figure, the current response for the two electrodes is almost identical. A similar behaviour was obtained in $100 \text{ mM K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{ H}_2\text{O} + 10 \text{ mM K}_3\text{Fe}(\text{CN})_6$ at pH 4; and $100 \text{ mM } (\text{NH}_4)_2(\text{FeSO}_4)_2 \cdot 6 \text{ H}_2\text{O} + 100 \text{ mM NH}_4(\text{FeSO}_4)_2 \cdot 12 \text{ H}_2\text{O}$ at pH 3 (not shown here). This investigation reveals that the reactivity of as-grown carbon electrodes is comparable to that of a platinum electrode. A similar study was reported by Zhu *et al.* [4] for boron doped diamond films grown by CVD, but their CVs were poorly defined, reflecting slow electrode reaction kinetics.

The electrochemical behaviour of as-grown carbon films in the aforesaid electrolytes were also investigated at scan rates of 16, 36, 49, 64 and 100 mV s^{-1}

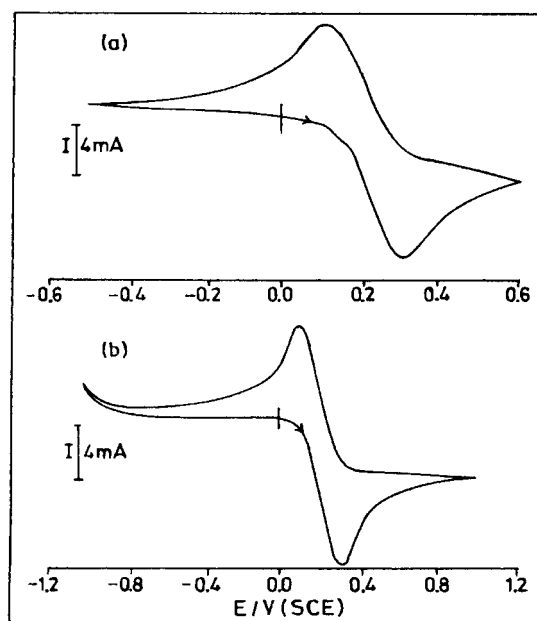


Fig. 5. Cyclic Voltammograms for (a) kerosene carbon and (b) Pt in $100 \text{ mM K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{ H}_2\text{O} + 10 \text{ mM K}_3\text{Fe}(\text{CN})_6$ at pH 9.2 (buffer). (Scan rate 50 mV s^{-1}).

and the anodic peak currents were plotted against the square root of scan rate. The response current was found to increase linearly with square root of the scan rate in all electrolytes. A typical plot is shown in Fig. 6. As-obtained straight lines indicate diffusion controlled electrode reactions at the carbon surface, similar to those at Pt electrode. The greater slope for carbon reconfirms its superiority over Pt in these experiments. It is, however, also possible that, although the geometrical area of both the electrodes is apparently equal, the effective area of the carbon film is greater due to uneven surface morphology, as observed in the SEM (Fig. 2).

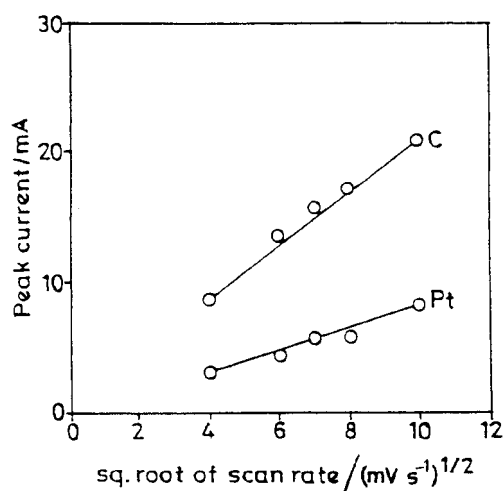


Fig. 6. Current responses of the kerosene carbon and platinum electrodes in $100 \text{ mM K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{ H}_2\text{O} + 10 \text{ mM K}_3\text{Fe}(\text{CN})_6$ at pH 9.2 (buffer) against square root of scan rate.

3.3. Application

The suitability of the kerosene-pyrolised carbon electrodes for application in the chlor-alkali industry was also examined. It was observed that these electrodes could be used to electrolyse 30% NaCl solution up to a current density of 300 mA cm^{-2} for more than 110 h of continuous operation without deterioration. In the chlor-alkali industry, very expensive, RuO_2 -treated titanium sheets are used for producing caustic soda. Our results suggest that kerosene-pyrolised carbon electrodes may have possible uses in this type of electrolysis.

4. Conclusion

Conducting carbon films obtained from the pyrolysis of kerosene vapour in argon atmosphere at 1000°C can be deposited over various ceramic materials of different size and can be used as an inert electrode in electrochemical studies. Its electrochemical window in aqueous solutions is larger than that of platinum. As-grown carbon films can be used as anode in the chlor-alkali industry to electrolyse brine solution at currents of 300 mA cm^{-2} . It is expected that the preparation of the kerosene carbon electrode can become commercially viable and may replace expensive glassy carbon electrodes.

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