# Synthesis of Graphite Films by Electrochemical Reduction of Hexachlorobuta-1,3-diene

**Hiroshi Nishihara,* Hiroshi Harada, Shigeru Kaneko, Masahiro Tateishi, and Kunitsugu Aramaki**
*Department of Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan*

Electrochemical reduction of hexachlorobuta-1,3-diene in aprotic solvents affords mostly graphitized films which can be easily doped with anions and also with cations.

Electropolymerization is a powerful tool for the synthesis of either electronically-conducting or redox-conducting polymer films. Our recent interests have focused on the synthesis of new kinds of conducting polymers by means of electrochemical reduction of halogenated compounds.[1] This paper presents an extension of this synthetic methodology, which is the first example of electrochemical graphitization.

Graphite films can be formed by electrochemical reduction of hexachlorobuta-1,3-diene (HCBD) in aprotic solvents. Figure 1 shows the cyclic voltammetry of HCBD at a glassy carbon electrode in 0.1 M $Bu_4NBF_4$–MeCN during the film formation. The continuous increase in size of the redox waves at −0.4 V *vs.* $Ag/Ag^+$ indicates the growth of an electroactive polymer film. The film attaches to the surface tightly when it is thin, but it can be separated from the electrode surface when it is thick and a positive potential (0.6 V) is applied after the film preparation. The film thus formed was black and its elemental composition was $C_4Cl_{0.3}$; however, the *X*-ray microanalysis indicated that the distribution of Cl was localized and the bulk of the film consisted of C.

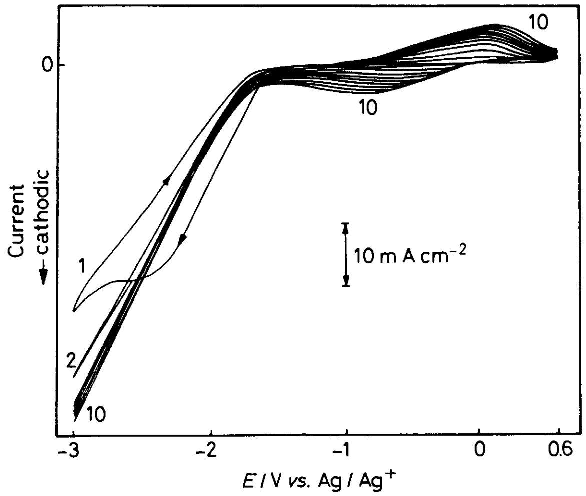

**Figure 1.** Cyclic voltammetry for reduction of HCBD (0.16 M) at a glassy carbon electrode in 0.1 M $Bu_4NBF_4$–MeCN at a scan rate of 0.15 V $s^{-1}$. Numbers in the figure refer to the number of cyclic scans.

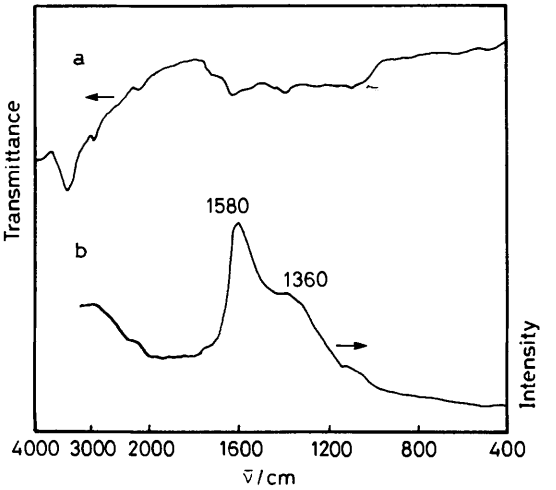

**Figure 2.** Infrared (a) and Raman (b) spectra of the film formed by electroreduction of HBCD.

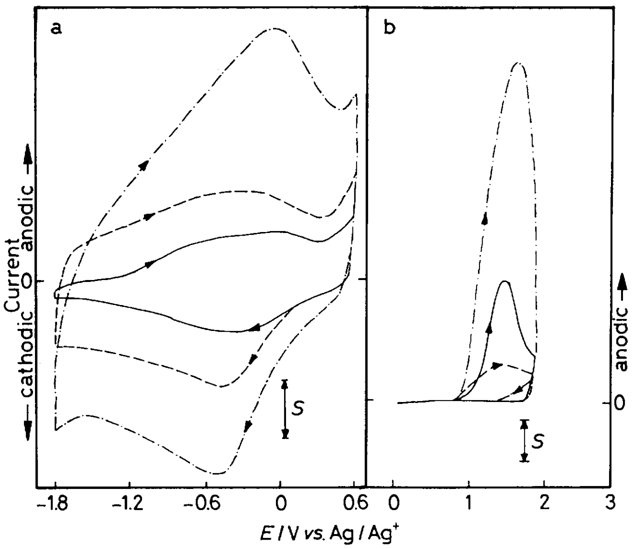

**Figure 3.** Cyclic voltammograms of the film formed from HBCD in MeCN with various electrolytes: (a) $Me_4NClO_4$ (– · – · –), $Et_4NClO_4$ (– – –), $Bu_4NClO_4$ (——); (b) $Me_4NBF_4$ (– · – · –), $Me_4NClO_4$ (——), $Me_4N(p\text{-}MeC_6H_4SO_3)$ (– – –). $S$ = 1 mA $cm^{-2}$.

The IR absorption spectrum of the film shows no significant peaks; however, in the Raman spectrum two strong bands are observed at 1580 and 1360 $cm^{-1}$ as shown in Figure 2. This suggests that the film is composed of graphite and the bands noted above are due to 'inner layer' graphite bound by two adjacent graphite planes and the $A_{1g}$ mode of $D_{6h}{}^4$ symmetry for small graphitic crystallites, respectively.[2] The graphite structure of the film was also confirmed by micro $X$-ray diffraction analysis.

Cyclic voltammetry of the film gives a reversible redox wave at $-0.4$ V vs. Ag/Ag$^+$ and an irreversible oxidation peak at 1.5 V. The peak currents of the redox wave at $-0.4$ V are affected by electrolyte cation size but not by anion size. (Figure 3a). On the other hand, the anodic peak at 1.5 V is influenced only by electrolyte anions (Figure 3b). These results suggest that the film can be doped with both cations and anions electrochemically. Change in the conductivity due to cation and anion doping was observed using a modified method of the twin electrode thin layer cell technique.[3] The undoped film has a conductivity of $10^{-6}$ S $cm^{-1}$, which increases up to 2—4 × $10^{-4}$ S $cm^{-1}$ on either cation doping or anion doping. This semiconducting film indicates that graphitization by the present electrochemical procedure is not complete, which is also supported by the broadness of the Raman peaks given in Figure 2. However, the procedure requires no high temperature treatment, and it is advantageous in the convenient synthesis of thin graphite films which are capable of facile anion and cation doping and can be attached tightly to various kinds of electrode materials.

We thank Professor R. W. Murray for useful advice on the conductivity measurements. This work was supported by a Grant in Aid for Scientific Research No. 62740264 from the Ministry of Education, Science and Culture (Japan).

*Received, 15th June 1989; Com. 9/02529D*

## References

1 H. Nishihara, M. Tateishi, K. Aramaki, T. Ohsawa, and O. Kimura, *Chem. Lett.*, 1987, 539; M. Tateishi, H. Nishihara, and K. Aramaki, *ibid.*, 1987, 1727; H. Nishihara, M. Noguchi, and K. Aramaki, *Inorg. Chem.*, 1987, **26**, 2862.

2 R. J. Bowling, R. T. Packard, and R. L. McCreery, *J. Am. Chem. Soc.*, 1989, **111**, 1217.

3 B. J. Feldman, P. Burgmayer, and R. W. Murray, *J. Am. Chem. Soc.*, 1985, **107**, 872.