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DURABLE CHIRAL GRAPHITE ELECTRODES MODIFIED CHEMICALLY WITH POLY(L-VALINE) AND POLY(N-ACRYLOYL-L-VALINE METHYL ESTER)[1]

Shigemitsu ABE and Tsutomu NONAKA*
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta,
Midori-ku, Yokohama 227

Graphite electrodes modified chemically with poly(L-valine) and poly(N-acryloyl-L-valine methyl ester) were prepared. They were remarkably more durable than the corresponding dip-coated electrodes when used repeatedly in the electrochemical asymmetric reduction of citraconic acid.

Poly(L-valine)-coated electrodes are effective electrodes with high asymmetric yields in electrochemical asymmetric reduction[2-4] and oxidation,[5] but their durability are not sufficient for repeated use.[3] In the present work, this disadvantage was overcome by binding L-valine units to graphite electrode surface through covalent bonds. Few reports dealing with so-called chemically modified polymer electrodes have been published,[6,7] and such modified electrodes for preparative electrolyses have not been reported.

Two kinds of graphite electrodes modified chemically with poly(L-valine) and poly(N-acryloyl-L-valine methyl ester) were prepared by the usual method for chemical modification of graphite surface (See Fig. 1, A_c and B_c). Electrode A_c: A graphite plate (4 x 2 cm) was first chemically modified with 1,3-diaminopropane by the method of Osa et al.[8] and then was treated for 3 d with L-valine N-carboxy anhydride[2] (1.0 g) in dry tetrahydrofuran (100 ml) containing a catalytic amount of triethylamine. Electrode B_c: Another graphite plate was first treated with thionyl chloride and then was treated for 1 d in dichloromethane (100 ml) containing triethylamine with poly(N-acryloyl-L-valine methyl ester) (1.0 g, $[\alpha]_D^{20}=-19°$), which was prepared by the graft-polymerization of the corresponding monomer[9] in the presence of 2,2'-azobisisobutyronitrile. Dip-coated electrodes[2] A and B were prepared by dipping graphite plates in 0.01 $g \cdot cm^{-3}$ trifluoroacetic acid and dichloromethane solutions of the respective polymers.

The electrochemical asymmetric reduction of citraconic acid was carried out by using these electrodes at pH 6.0. Experimental procedures were similar to those of previous works.[2,3]

As shown in Fig. 2, the chemically modified electrodes (A_c and B_c) were much more durable than the corresponding dip-coated electrodes (A and B). The electrode A_c gave lower asymmetric yields than the electrode A in the initial use and the first reuse. The lower yields may be attributed to smaller amounts of poly(L-valine) on the electrode A_c surface and may be improved by changing conditions for the graft-polymerization. From results obtained in this work, it is suggested that the chemical modification of electrodes with polymers is an excellent method to prepare durable polymer electrodes suitable for preparative electrolyses.

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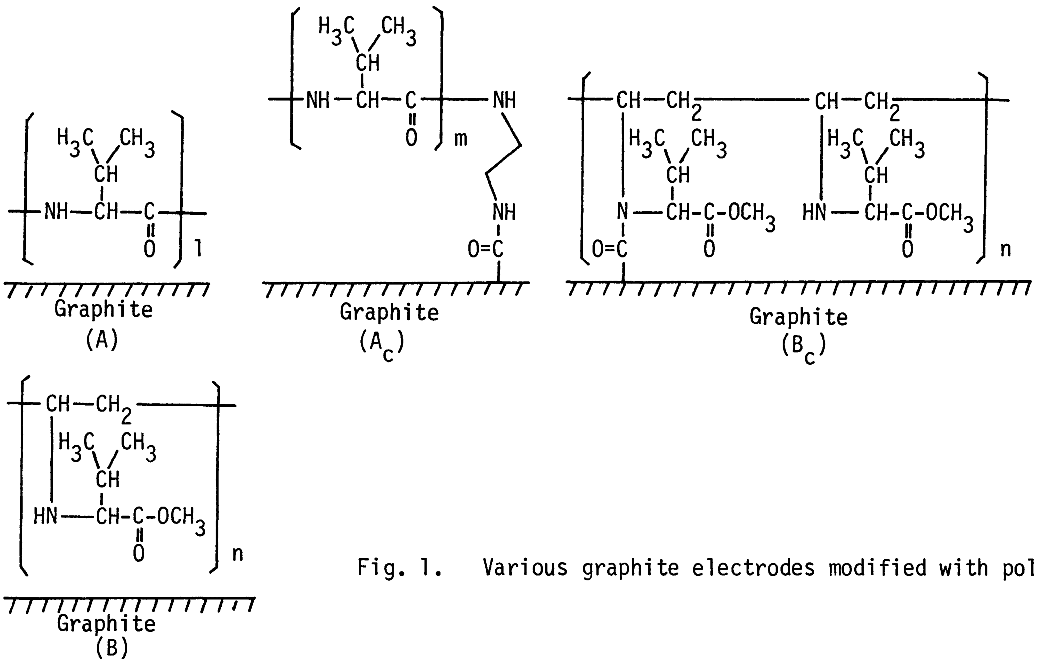

Fig. 1. Various graphite electrodes modified with polymers.

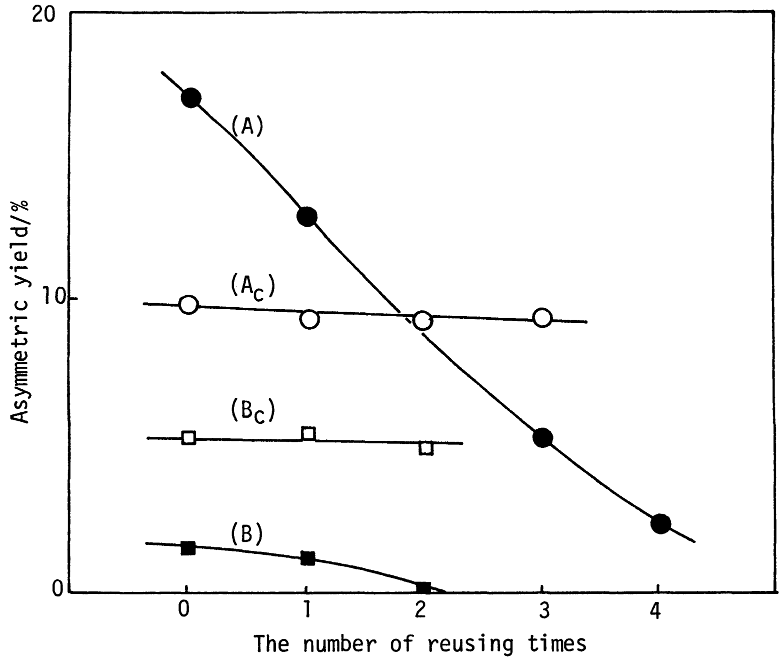

Fig. 2. Asymmetric reduction of citraconic acid to methylsuccinic acid on reused graphite electrodes modified with polymers.

A: Dip-coated with poly(L-valine), A_c: chemically modified with the same,
B: dip-coated with poly(N-acryloyl-L-valine methyl ester), B_c: chemically modified with the same.

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