Electroorganic Synthesis Using Boron-Doped Diamond Electrodes

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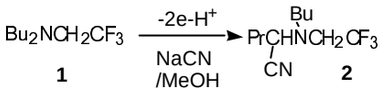
The development of novel types of durable and environmentally friendly electrode materials is necessary from viewpoints green chemistry and economics. In this respect, boron-doped diamond thin films (BDD) have recently attracted much attention as a new electrode material. BDD electrodes have unique electrochemical properties such as a wide potential window, chemical and physical stability, and small background current, etc. In spite of these excellent properties, BDD electrodes have received little attention in electroorganic synthesis so far.

With these in mind, anodic substitution reactions were comparatively studied using BDD, Pt and GC anodes in this work.

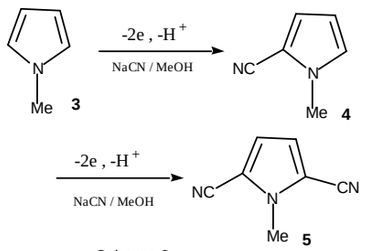
Firstly, anodic cyanation of aliphatic amines such as 2,2,2-trifluoroethylamine **1** was carried out in 0.4 M NaCN/MeOH using BDD, Pt, and GC electrodes. The BDD electrodes as well as a Pt electrode provided the corresponding α-cyanoamine with good current efficiency as shown in Scheme 1. In sharp contrast, GC anode did not give any cyanated product.



C. Eff. BDD: 77%
Pt : 75%
GC : 0%

Scheme 1

Next, anodic cyanation of 1-methylpyrrole (**3**) was carried out similarly.



Scheme 2

Figs. 1-3 show I-E curves of **3** at BDD, GC, and Pt anodes, respectively.

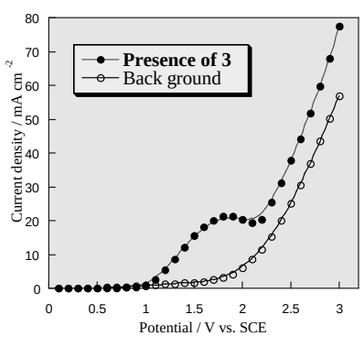


Fig. 1

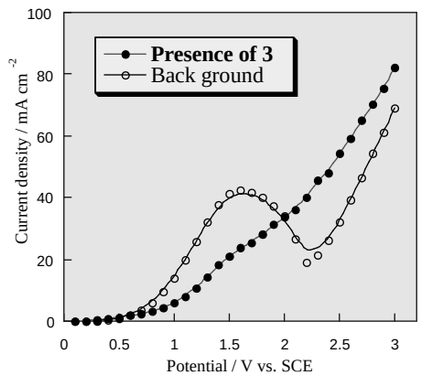


Fig. 2

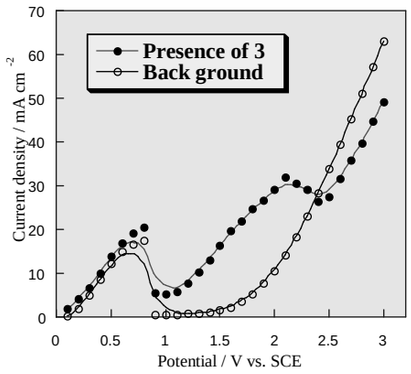


Fig. 3

Constant current anodic cyanation of **3** gave mono-and dicynation products **4** and **5** as shown in Scheme 2. Good to high total current efficiencies for mono- and dicyanation were obtained at BDD and Pt anodes, while GC anode provided poor current efficiency as shown in Fig. 4. In addition, high selectivity for monocyanation was achieved using BDD and Pt anodes even at high current density, while the use of GC anode resulted in lower selectivity.

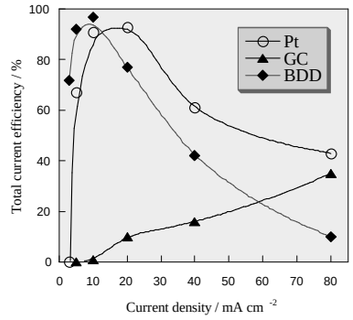


Fig. 4

Furthermore, we have achieved anodic methoxylation and acetoxylation, and fluorination of organosulfur compounds using BDD anodes.

Thus, anodic substitution reactions using BDD electrodes were successfully carried out. These results clearly indicate that BDD electrodes are promising new valuable electrode materials for electoorganic synthesis.