Boron-doped Diamond as a Quasi-reference Electrode

Zhen Peng[1], Andrea Fiorani[1], Kazumi Akai[1], Michio Murata[1], Atsushi Otake[1], and Yasuaki Einaga[1]
[1] *Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan*
Corresponding author: einaga@chem.keio.ac.jp

1. Introduction

Commercial reference electrodes (RE), such as silver/silver chloride (Ag/AgCl), and mercury/calomel ($Hg/HgCl_2$), are commonly used in electrochemical systems to achieve accurate potential control of the working electrode (WE). However, these electrodes suffer from several drawbacks, including difficulties in miniaturization, electrolyte leakage, and the toxicity of Ag^+/Hg^{2+} to biosystems. Boron-doped diamond (BDD) is a carbon-based electrode that is biocompatible and has been comprehensively investigated as a WE. Besides, other unique properties, such as surface chemical inertness, wide potential window, and accessible modulation of its shape, may contribute to its excellent performance as a quasi-RE (QRE). However, the reasons behind it have yet to be noticed, for example, the mechanism that ensures potential stability, and the factors that establish such potentials, which is thus hoped to be disclosed in this work.

2. Experiment

Four BDD electrodes with different boron concentrations (1% and 0.1%), and different surface terminations (hydrogen (H-T) and oxygen (O-T)) were first investigated in order to elucidate the fundamental aspects. Their stability was evaluated by the open circuit potential (OCP) measurements and further verified by cyclic voltammetry tests in 0.1 mM $K_3[Fe(CN)_6]$/1M KCl before and after OCP. In addition, the effects of pH and the electrolyte nature (phosphate buffer solution, PB) on OCP were discussed by a comparison of OCP and capacitance measured by impedance analysis. The final assessment of the QRE-BDD was made by monitoring the variations of the half-wave potential of a redox couple, namely 0.1 mM $[Fe(CN)_6]^{3-/4-}$/ 1 M KCl. Finally, the optimized BDD was used as a QRE and coupled with two identical BDD electrodes to form an all-BDD three-electrode system, which was assessed for its practical application in the detection of free chlorine, a strong oxidant, or dopamine, an important neurotransmitter.

3. Conclusion

Compared to doped boron concentration, surface termination plays a more critical role in the stability and the definition of the potential. Specifically, the QRE-BDD with an H-T surface exhibits a smaller variety and a lower OCP than those with an O-T surface doped with the same boron concentration. 1% BDD with an H-T surface (1% BDD H-T) is examined as the best QRE by showing lower than 0.1 V of potential drift over a period of 6000s during OCP tests and a negligible shift of 3.7 mV for the $E_{1/2}$ of $[Fe(CN)_6]^{3-}$. (Fig.1) The OCP is found to be affected by the interaction between the H-T surface and the anions or protons. It is confirmed by changes in the differential capacitance as a function of electrolyte concentration, anion species and pH, which were affected by specific adsorption on the positively charged H-T surface. (Table 1)

The effect of $[Fe(CN)_6]^{3-}$ was demonstrated to only impose on the potential of the QRE-BDD, but had no effect on its stability. And the maximum drift for 60 CV cycles over 3 days is as small as 0.037 V, verifying its excellent long-term stability. The practical application as a QRE of a 1% BDD H-T electrode was assessed by the detection of free chlorine and dopamine, which displays an excellent linear response (R^2>0.99).

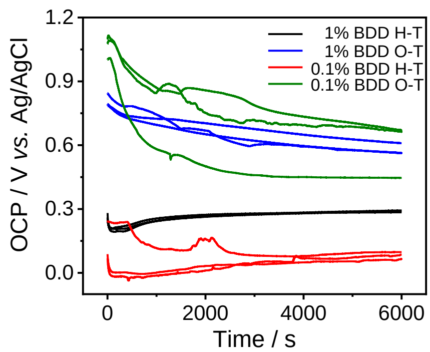

Fig. 1.OCP comparison in 3M KCl.

Table. 2. Molar ratio of phosphate species[3] and the differential capacitance (C_d) of BDD H-T in 0.1 M phosphate buffer solutions at different pH.

	pH=3.65	*pH=6.86*	*pH=10.85*
H_3PO_4	*0.02*	-	-
$H_2PO_4^-$	*0.98*	*0.69*	-
HPO_4^{2-}	-	*0.31*	*0.97*
PO_4^{3-}	-	-	*0.03*
C_d /μF cm^{-2}	*0.08*	*0.12*	*0.20*

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