Preparation of boron-doped diamond modified by bimetal nickel and zinc

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Abstract. Nickel has been known as a good catalyst due to its high activity and stability, but the potential formation of NiOOH is quite high. In this work, zinc together with nickel was used to modify the surface of boron-doped diamond (BDD) to lower the formation potential of NiOOH. Electro-deposition (multi pulse amperometry) technique was applied at a potential of -1.6 V for 600 s. The prepared electrode (NiZn-BDD) characterized using SEM-EDX and XPS shows that both nickel and zinc were deposited homogenously on the surface of BDD with the ratio of 1:2 for nickel:zinc.

Keywords: Nickel, zinc, boron-doped diamond, surface modification

1. Introduction
Nickel, a low-cost metal, has been known for its high activity and stability. However, it is reported that nickel has a high over-potential or formation potential of NiOOH, an active catalyst species of nickel [1]. Hence, another metal doping, such as cobalt, zinc, cadmium and manganese, is needed to lower the formation potential of NiOOH [2]. On the other hand, boron-doped diamond (BDD) has been known for its wide potential window, high stability and good durability compared to other conventional electrodes [3].

Nickel-zinc bimetallic has been known for its good characteristics and can be used in many application fields, such as for corrosion protection of steel [4], electrochemical decomposition of urea [5], and for methanol oxidation in alkaline medium [6]. The preparation of nickel-zinc deposited onto BDD is further explained in this work.

The aim of this work is to study the electrodeposition of nickel and zinc deposited on the surface of the BDD using electrodeposition (multi pulse amperometry) technique. The prepared electrode was then characterized using SEM-EDX and XPS to further confirm the nickel and zinc particles’ distribution on the surface of BDD.
2. Experimental

2.1. Preparation of NiZn-BDD
BDD 1% was fabricated by applying a microwave plasma-assisted chemical vapor deposition system (MPCVD, CORNES Technologies/ ASTeX-5400) [7]. To prepare NiZn-BDD, 40 mM nickel solution was prepared by adding 0.58 g of Ni(NO₃)₂·6H₂O to 50 mL buffer acetate pH 5 and 40 mM zinc solution was prepared by adding 0.136 g of ZnCl₂·6H₂O to 25 mL buffer acetate pH 5. The bimetal NiZn solution was prepared by mixing the 40 mM nickel solution and 40 mM zinc solution by the ratio of 4:1. The bimetal NiZn was then deposited onto the surface of BDD using chronoamperometry deposition technique at a potential -1.6 V for 600 s.

2.2. Characterization of NiZn-BDD
The NiZn-BDD electrode was then characterized using scanning electron microscopy (SEM, JCM-6000, JEOL) and X-Ray photoelectron spectroscopy (XPS, JPS-9010TR, JEOL).

3. Results and discussion
Nickel and zinc have been deposited using chrono-amperometry deposition technique. The deposition potential is set at -1.6 V to give enough reduction potential for both nickel and zinc particles to be deposited onto the surface of BDD. Nickel could be deposited on the surface of BDD into two forms through the electrodeposition technique: (1) as nickel metal and (2) nickel hydroxide [8, 9]:

\[
\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0 \tag{1}
\]

\[
\text{Ni}^{2+} + 2OH^- \rightarrow \text{Ni(OH)}_2 \tag{2}
\]

whereas zinc has been deposited into Zn⁰ on the surface of BDD through the electrodeposition technique [8]:

\[
\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}^0 \tag{3}
\]

The prepared electrode was further characterized using SEM-EDX. Figure 1 shows SEM images of bare BDD (a) and NiZn-BDD (b). As shown in figure 1, the nickel and zinc particles were deposited quite homogenously on the surface of the BDD. The EDX spectra in figure 2 shows the distribution of

![Figure 1. SEM images of (a) bare BDD and (b) NiZn-BDD.](image-url)
nickel and zinc particles on the surface of the BDD. The figure implies that both nickel and zinc particles have been deposited on the surface of BDD with the atomic ratio of nickel:zinc is 1:1 according to the EDX result shown in table 1.

Figure 2. EDX images of NiZn-BDD.

Table 1. EDX characterization of NiZn-BDD.

|         | Nickel | Zinc | Carbon |
|---------|--------|------|--------|
| % mass  | % atomic | % mass  | % atomic | % mass  | % atomic |
| 35.80   | 17.65  | 36.77 | 16.28  | 27.43  | 66.08    |
Figure 3. XPS wide spectra of (a) NiZn-BDD, (b) narrow spectra of nickel, and (c) narrow spectra of zinc.

The prepared electrode was then further characterized by XPS as shown in figure 3. The characteristic of metallic nickel of Ni_{2p3/2} was detected at the binding energy (BE) of 851.63 eV and Ni(OH)\textsubscript{2} was found at the binding energy of 855.87 eV and 861.18 eV (figure 3b). From figure 3c, it is found the characteristic of metallic zinc of Zn_{2p3/2} at the binding energy (BE) of 1021.96 eV. It is implying that nickel in the form of nickel metal and nickel hydroxide, and zinc in the form of zinc metal have been fully deposited on the surface of BDD at a potential of -1.6 V. The SEM-EDX and XPS characterization conclude that both particles of nickel and zinc have been successfully deposited on the surface of BDD.

4. Conclusion
NiZn particles has been successfully deposited homogenously onto the surface of BDD. SEM-EDX characterization showed the distribution of nickel and zinc particle on the surface of BDD and the ratio obtained from EDX characterization is 1:1 for nickel:zinc. XPS characterization was further confirmed that both nickel and zinc particle was deposited on the BDD surface.
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