Enhanced Mass Activity and Stability of Bimetallic Pd-Ni Nanoparticles on Boron-Doped Diamond for Direct Ethanol Fuel Cell Applications

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Abstract: In this work, electrochemical deposition of Pd (palladium) and bimetallic Pd-Ni (nickel) nanoparticles on oxygen-terminated boron-doped diamond (BDD) is described for use in direct ethanol fuel cell. A potentiostatic two-step electrochemical method involving the electrodeposition of Ni nanoparticles followed by mono-dispersed Pd nanoparticles on oxygen-terminated BDD substrate was used for the fabrication of Pd-Ni/BDD electrode. The modification of BDD with the bimetallic Pd-Ni nanoparticles led to the synergistic effects of the electron interaction at the metallic interfaces and thus higher electrochemical activity was achieved. The electrocatalytic activity of the bimetallic Pd-Ni nanoparticles was evaluated in an alkaline solution containing ethanol and compared to that of the Pd nanoparticles alone. The bimetallic Pd-Ni nanoparticles showed 2.4 times higher mass activity than the similar systems from literature as well as stability when operated in alkaline media. Higher electrochemical response towards the electrooxidation of ethanol observed for the bimetallic electrocatalysts was due to the synergistic effects of the electron interaction at the interface of the two metals. Chronopotentiometric measurements revealed that Pd is more stable when anchored to the Ni nanoparticles towards the electrooxidation of ethanol. The optimised loading of mono-dispersed Pd on a foreign Ni metal as nanoparticles plays a crucial role in achieving a high mass (3.63 x 10^6 mA/g) and specific (10.53 mA/cm^2) electrocatalytic activity of Pd towards ethanol electrooxidation. The synthesised bimetallic electrocatalysts of this research also possess a higher stability towards ethanol electrooxidation in alkaline media.

1. Introduction

Fuel cell are receiving increasing attention in recent years due to their ability to increase overall energy efficiency. The direct alcohol alkaline fuel cell (DAAFC) subcategory has attracted signficant research efforts because of the possibility to use non-noble materials, which are more stable in alkaline media and thus, reduce the noble metal content, the main cost component of the electrocatalysts. The DAAFC is able to convert the chemical energy stored in the fuel (i.e. alcohol) into electricity directly and therefore, can be used as the power source in portable electronics, transportation and other emerging applications.[1–4]

Hybrid materials, consisting of graphitic nanostructures (carbon nanotubes or graphene, for instance) and various metal particles have been widely studied as functional components in catalysis and fuel cell applications.[4–6] BDD is an alternative carbon substrate due to its unique features, such as wide potential window, low background capacitive current, chemical stability and robustness under hostile environments (potential, temperature, pressure), which have been described further in previous reports.[7–14] Diamond electrodes can be modified by metal nanoparticles enhancing its sensitivity towards various analytes compared to the unmodified electrode.[7,15] Of note is the resistance of diamond to electrocorrosion, a fact which make it attractive especially in the field of fuel cell.[16–18] Pt is one of the most effective electrocatalysts and used widely; nevertheless, the high cost as well as its tendency to be poisoned by the reaction intermediates during the ethanol electrooxidation can be prohibitive for future use.[19,20] Because of the aforementioned reason, core-shell structures[8,21–26] and the embodiment of non-noble metals[8,23,27] promise to enhance the stability of the electrocatalysts in DAAFC as well as to reduce their cost. One of the challenges in this field is also the development of efficient electrocatalysts capable to produce CO_2 after the ethanol electrooxidation or in other words to cleave the C-C bonds.[28] Pd has shown recently that can be more active, stable and poison tolerant towards the intermediates of ethanol electrooxidation species.[29–32] Furthermore, Pd is 50 times more earth abundant than its counterpart Pt and is a promising candidate to replace the latter in the field of alkaline fuel cell.[33]

In the present study, the modification of oxygen-terminated BDD electrodes with Pd and Pd-Ni nanoparticles is proposed for ethanol oxidation of relevance to the direct ethanol alkaline fuel cell (DEAFC). The motivation for this work is ultimately the continuation of our understanding of how metallic interfaces formed on the Ni nanoparticles agglomerate with partial coverage of mono-dispersed Pd nanoparticles behave on diamond by comparison with similar structures on other forms of carbon.[8] The second objective of this study is to gain a further understanding of how different core metals behave on diamond and how they can affect the stability, electrochemical activity and finally the poison tolerance towards the by-products of ethanol electrooxidation. In both of these cases, the electrochemical modifications introduced by the electrodeposition of the metal nanoparticles reflect the particular properties of the metal, the interface interaction between the two metals and their interaction with the underlying diamond.

2. Results and Discussion

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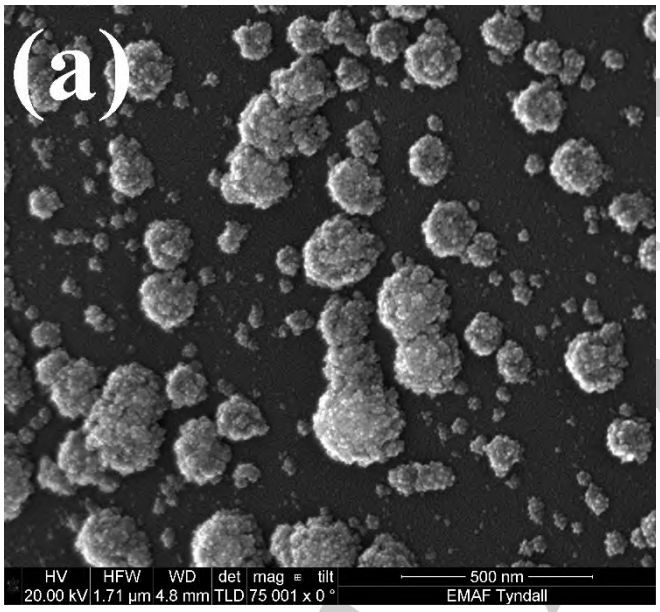
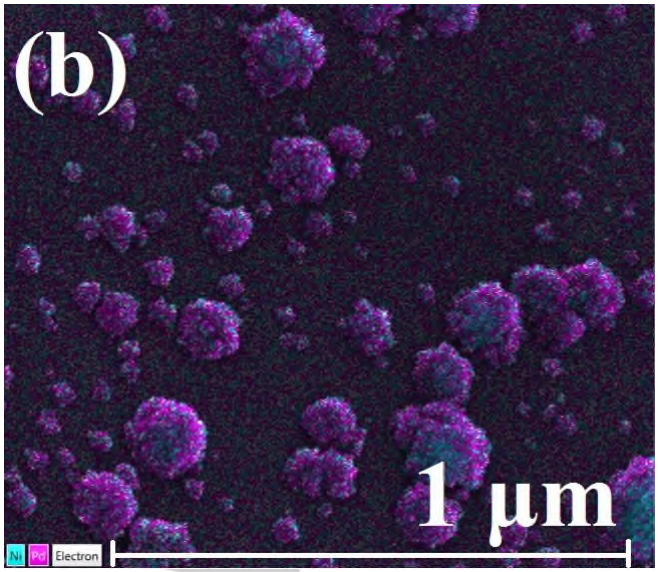
2.1 Morphology, EDX and XPS Characterisation of the Deposits on BDD Electrode

The morphology of the deposits was characterised by a scanning electron microscope and the images are shown in Fig. 1 (a-b). Ni particles have been deposited in a non-uniform manner along the diamond edges with visible agglomeration as can be seen from the Figure 1(a) due to the high metal loading (658 mC/cm^2). The size of the Ni particles cannot be estimated due to the latter effect. The lateral conductivity of diamond as well as the non-uniform distribution of the B dopant led to the non-uniform distribution of the deposits as reported previously.[8] The sequential deposition of Pd onto Ni produced smaller particles around 13 nm as shown in elemental mapping of Figure 1(b). The elemental mapping provides information for the deposition of the Pd-Ni nanoparticles in which Pd nanoparticles quite sparsely cover the Ni particles. The elemental composition of the electrodes is displayed in Figure 1(c). Energy dispersive x-ray spectra shows slightly more intense Ni peaks than the Pd as expected from the low amount of Pd metal loading by comparison with Ni.





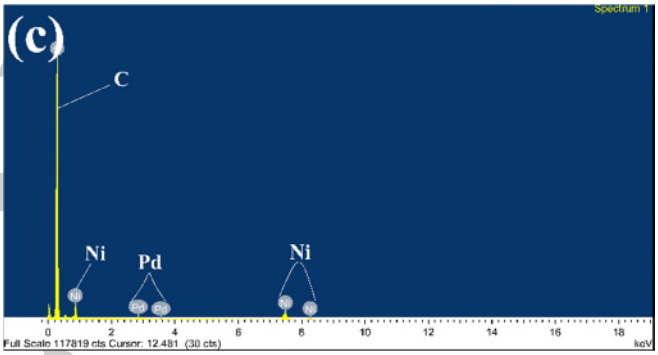


Figure 1. (a) SEM image of Ni deposited on BDD electrodes. (b) Elemental mapping of Pd-Ni deposited on BDD showing Ni nanoparticles agglomerate with partial coverage of mono-dispersed Pd nanoparticles. (c) EDX spectra of the Pd-Ni nanoparticles on BDD electrode.

The elemental composition as well as chemical and electronic states were explored by x-ray photoelectron spectroscopy as shown form the XPS spectra in Figure 2. Figure 2 (a) shows the wide scan survey of the oxygen-terminated BDD electrodes with the relevant elements of Ni, Pd and Pd-Ni. The wide scan survey illustrates the existence of C, O and the relevant peaks of the main metals. Figure 2 (b) illustrates the Ni 2p peaks of the Ni/BDD and Pd-Ni/BDD electrodes. The Ni modified BDD has Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks at 856.6 eV and 874.5 eV, respectively.[34] The Ni photoelectron peak of the Pd-Ni/BDD electrode is attenuated significantly. As has been reported in previous work[8] the most likely scenario is that the Pd has covered the underlying Ni. The Pd modified BDD has two main peaks, the Pd $3d_{5/2}$ at 336.4 eV and Pd $3d_{3/2}$ at 341.7 eV, respectively. The Pd photoelectron peak of the bimetallic electrode has the same peaks. There is a binding energy shift of 0.2 eV, which implies an electronic interaction between the two metals. The negative shift of binding energy can be attributed to the increase in interfacial charge of Pd atoms relative to the bulk