



# Investigation of the porous nanostructured Cu/Ni/AuNi electrode for sodium borohydride electrooxidation



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## ABSTRACT

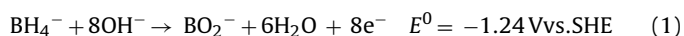
An electrochemical approach to nanostructured Cu/Ni/AuNi catalyst design using the electrodeposition process followed by galvanic replacement technique is presented. The procedure consisted of the electrodeposition of Ni–Zn on the Ni coating with subsequent replacement of the zinc by gold at open circuit potential in a gold containing alkaline solution. The surface morphologies and compositions of coatings were determined by energy dispersive X-ray and scanning electron microscopy techniques. The results showed that the Cu/Ni/AuNi coatings were porous composing of discrete Au nanoparticles. The electrocatalytic activity of Cu/Ni/AuNi electrodes for sodium borohydride electro-oxidation was studied using cyclic voltammetry, chronoamperometry, chronopotentiometry and electrochemical impedance spectroscopy techniques. The electro-oxidation current on Cu/Ni/AuNi catalyst is much higher than that on flat Au catalyst. The onset potential and peak potential on Cu/Ni/AuNi catalysts are more negative than that on flat Au catalyst for borohydride electrooxidation. The impedance behavior also shows different patterns, capacitive, and negative resistances and inductive loops at different applied anodic potentials. All results show that the Cu/Ni/AuNi catalysts can be applied as potential anode catalysts for the direct borohydride fuel cells.

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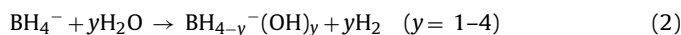
## 1. Introduction

The increasing demand for efficient and clean power sources has greatly stimulated the research and development of low-temperature fuel cells for stationary and mobile applications [1,2]. Several promising fuels, e.g. hydrogen and methanol, have been intensively evaluated and concerns in poisoning, supply and storage, capacity and efficiency, toxicity were raised [1–4]. In recent years, aqueous solution of sodium borohydride has been widely studied as fuel in direct borohydride fuel cell (DBFC). The fuel (borohydride salt), also presents several advantages: it is non-toxic, can easily be stored and relatively stable in alkaline solution, while exhibits rather high energy density ( $9.3 \text{ Wh g}^{-1}$  at 1.64 V) [5–8]. Borohydride fuel cells are currently under active investigation as part of worldwide efforts to develop environmentally sustainable sources of power [7–12].

The oxidation reaction of borohydride can take place with an eight-electron process described as follows (Eq. (1)) [13]:



However, this reaction is barely found to happen in practice because the anodic reactions on the electrodes have to compete with the hydrolysis reaction. The hydrolysis of borohydride ion produces hydrogen gas and a number of borohydroxide or oxide intermediates that deplete the amount of borohydride ions available for oxidation (Eq. (2)) [14,15].



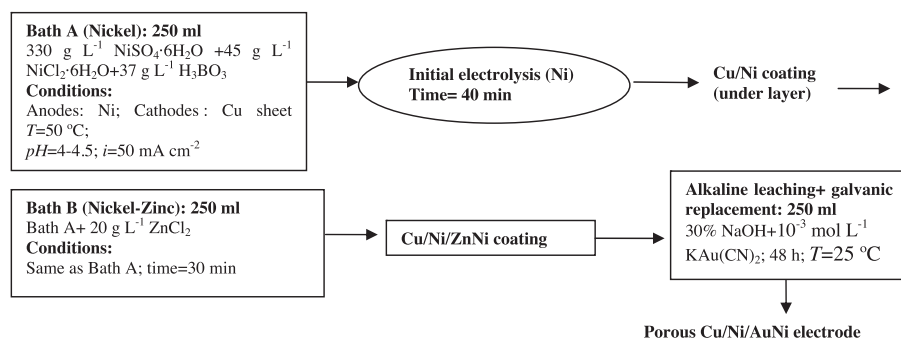
The electrochemical reaction of borohydride depends on the catalysts material, alkaline solution concentration and also on temperature.

Pt- or Au-based binary electrocatalysts tested in reactions relevant to fuel cell technology (oxygen reduction [16,17]; methanol oxidation [18,19]; borohydride oxidation [20]) constitute a large part of recent electrochemical literature.

The galvanic replacement procedure provides a very simple and effective method to prepare porous bimetallic nanostructures having a lower standard electrode potential compared to that of the target material.

In this work, we demonstrate a procedure for synthesizing porous Cu/Ni/AuNi nanostructures via galvanic exchange reaction using Zn from Cu/Ni/ZnNi coating. NiZn coating was grown on Ni by electrodeposition technique and Cu/Ni/ZnNi electrode was obtained. Porous Cu/Ni/AuNi nanostructures were produced by exposing the Cu/Ni/ZnNi electrode to an alkaline aqueous solution

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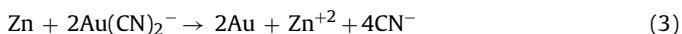
**Fig. 1.** Flowchart of typical preparation procedure for the nanostructured Cu/Ni/AuNi electrodes.

of the corresponding gold salt ( $10^{-3} \text{ mol L}^{-1} \text{ KAu(CN)}_2 + 30 \text{ wt.}\% \text{ NaOH}$ ). These porous nanostructures are stable under ambient conditions and show a highly porous catalytic surface suitable for the electrooxidation of borohydride in alkaline solution.

## 2. Experimental

All reagents used in this work were of analytical grade provided by Merck were used without further purification. All solutions were prepared using double distilled water. The Cu/Ni/AuNi catalysts were prepared through the electrodeposition and galvanic replacement processes. A typical preparation procedure for the nanostructured Cu/Ni/AuNi electrode is presented in Fig. 1. In detail, the copper substrates (cathodes) were cut and mounted in polyester resin except a surface area of  $1 \text{ cm}^2$  for measurements. Electrical conductivity was provided by soldering a copper wire. Before electrodeposition, the electrode surfaces were polished with emery paper (2500 grit size), then washed with double distilled water, thoroughly degreased in a 30 wt.% NaOH solution for 5 min, washed again with distilled water, dipped into 10 wt.%  $\text{H}_2\text{SO}_4$  solution for 1 min followed by a rinse with distilled water and immersed in the bath solution. The plating baths and conditions used for the smooth Ni and Cu/Ni/ZnNi coatings are given in Fig. 1. After deposition, the electrodes were rinsed with distilled water in order to remove residues of bath chemicals and unattached particles. The Au deposition was performed simply by immersing the Cu/Ni/ZnNi electrode into a 30 wt.% NaOH solution of  $\text{KAu(CN)}_2$  salt (Merck, 99.99%) with concentration of  $10^{-3} \text{ mol L}^{-1}$  for 48 h at room temperature.

The standard reduction potential of the  $\text{Au}^+/\text{Au}$  pair (1.691 V vs. SHE) is higher than reduction potential of the  $\text{Zn}^{2+}/\text{Zn}$  pair ( $-0.762 \text{ V}$  vs. SHE), and it can be reduced by Zn as shown in the following equation:



Finally, the electrode was removed from the solution and washed with double distilled water thoroughly. The surface composition and morphology of electrodes before and after galvanic replacement were determined using scanning electron microscopy (SEM, Philips, and Model XL30) equipped with an energy dispersive X-ray (EDX) spectrometer.

The electrochemical studies were carried out in a conventional three-electrode electrochemical cell and all the solutions were purged with purified nitrogen for 10 min before the measurements. A platinum sheet of the geometric area of about  $20 \text{ cm}^2$  was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel electrode (SCE). Cyclic voltammetry (CV), chronoamperometry, chronopotentiometry and electrochemical impedance spectroscopy (EIS) experiments were performed using a Princeton Applied Research, EG&G PARSTAT

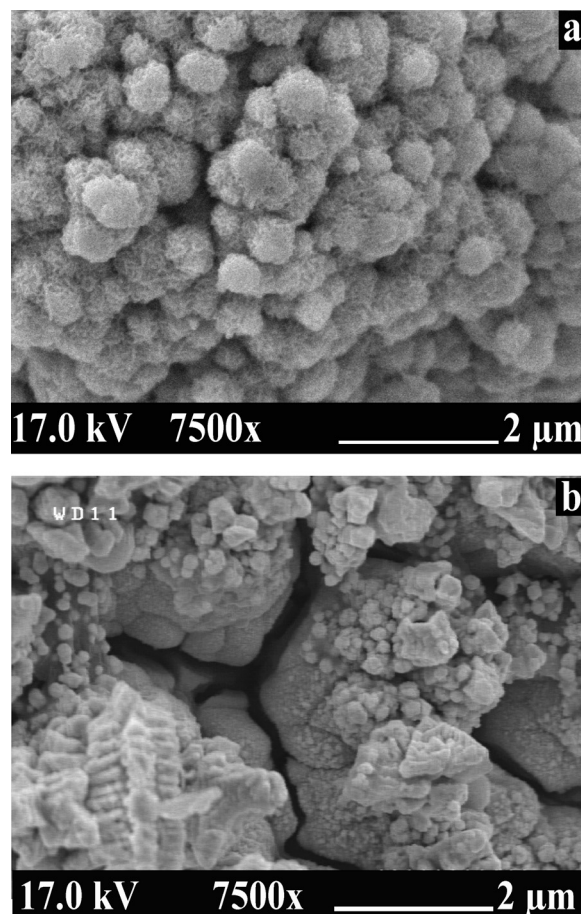
2263 Advanced Electrochemical system run by PowerSuite software.

The impedance spectra were recorded in a frequency range of 100 kHz to 10 mHz, with the amplitude (r.m.s. value) of the ac signal being 10 mV. The acquired data were curve fitted and analyzed using ZView(II) software.

## 3. Results and discussion

### 3.1. Characterization of coatings

The SEM images of Cu/Ni/ZnNi electrode and Cu/Ni/AuNi electrode are given in Fig. 2. It can be seen from Fig. 2a that the surface



**Fig. 2.** SEM images of (a) Cu/Ni/ZnNi coating and (b) Cu/Ni/AuNi coating after leaching-galvanic replacement process.

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