Implantable nonenzymatic glucose/O₂ micro film fuel cells assembled with hierarchical AuZn electrodes

Hui-Bog Noh,∗ M. Halappa Naveen,∗ Yong-Jin Choi,∗ Eun Sang Choe∗ and Yoon-Bo Shim∗∗

Hierarchical AuZn dendrites revealed electrocatalytic properties towards the glucose oxidation and the four-electron O₂ reduction. The micro fuel cell using AuZn electrodes generated a power density of 2.07 and 0.29 mW cm⁻² for glucose and human whole blood. The micro film fuel cell implanted into the rat brain produced ~0.52 V continuously operating for more than 18 days.

Biomass is an ideal alternative to fossil fuels.¹ Of these, glucose is one of the most interesting biomass fuels, because it is renewable, cheap, abundant, non-toxic, non-flammable, and can be easily handled and obtained. Furthermore, it is an excellent candidate fuel for implantable fuel cells (FCs) in animal bodies and body fluids.²,³ Attempts have been made to investigate implantable glucose biofuel cells (BFCs) based on enzyme catalysts, such as glucose oxidase,⁴,⁵ although such FCs have exhibited insufficient durability and lack of reproducibility of the enzymatic systems. Although the lifetime of enzyme based BFCs can be somewhat enhanced using conducting-polymer-based enzyme electrodes,⁶ it is expected that FCs driven by nonenzymatic oxidation of glucose will be more useful. However, the methods developed for nonenzymatic glucose oxidation suffer from two fundamental problems.⁷ One is due to the low efficiency of the oxidation reaction caused by slow rates, and the other is associated with electrode surface poisoning by adsorbed intermediates or products.⁸ Thus, they are difficult to be used as a continuous power source. Consequently, the development of new electrode materials that can efficiently catalyze the glucose oxidation and the oxygen reduction in mammals is an important goal of current implantable BFC studies. Recently, metal dendrites have received extensive attention in the fields of biology, chemistry, and physics owing to their unique geometry and potential applications in FCs⁹⁻¹² and biosensors.¹³,¹⁴ Although numerous metals have been employed to generate dendrites,¹¹,¹² the applications of hierarchical AuZn as FC and BFC electrodes have not been reported much, so far. The aim of the present study is to synthesize new hierarchical bimetal catalysts (AuZn, AuNi, and AuCo) and apply them to the implantable glucose/O₂ FCs (GOFCs).

AuZn, AuNi, and AuCo dendrites were electrochemically prepared, their preparation conditions and analytical parameters were optimized, and the catalytic activity of fuel cell reactions was analyzed [see ESI† Materials and Methods section]. Among these bimetal dendrites, the AuZn dendrite was extensively studied, because it showed the best performance in the FC reactions compared with the other Au-transition metal bimetals. The AuZn dendrite was prepared under the following optimized conditions: the dendrites were prepared in an O₂ purged 0.1 M Na₂SO₄ solution containing 10.0 mM HAuCl₄·3H₂O and 30.0 mM ZnCl₂, NiSO₄, and CoCl₂·4H₂O, respectively. The pH was maintained at 4.0 using NaOH. The deposition potentials for AuZn, AuNi, and AuCo dendrites were –500.0, –600.0, and –700.0 mV, respectively, for 1000.0 s. The mixed solution was purged with N₂ gas for 30 min before the electodeposition process. Then, the electrodes were washed successively with 0.1 M HCl, acetone, ethanol, and water several times. The experimental parameters were optimized in terms of the concentration of analytes, deposition time, deposition potential, and pH, which affect dendrite formation and catalytic activity.

Since the surface morphologies of all as-prepared bimetals are the same, that of the AuZn bimetal electrode is discussed as a typical example based on scanning electron microscopy (SEM) in the present study, as shown in Fig. 1(A), which is distinguished by the presence of side branch tips split from the main chain (images of AuNi and AuCo are not shown). Simultaneously, energy dispersive X-ray spectroscopy (EDX) analysis was also performed to determine the composition of the AuZn dendrite. The spectrum displayed in Fig. 1(B) (where the inset is an SEM image of the sample) shows that the ratio of the atomic components of the...
bimetal, Au : Zn, is 51.88:48.12. To obtain further information on the distribution of Au and Zn during the dendrite growth, spectra and images were acquired using time-of-flight secondary ion mass spectroscopy (TOF-SIMS) in a positive mode. Fig. 1(C) shows the TOF-SIMS images of the dendrite for (a) Au\(^{3+}\) (m/z 590.90), (b) Zn\(^{2+}\) (m/z 130.84), and (c) overlaid Au\(^{3+}\) and Zn\(^{2+}\) ions. Au\(^{3+}\) and Zn\(^{2+}\) were chosen due to their obvious signals, and these TOF-SIMS images present similar topographies and morphologies to those observed in the SEM image. In this case, the analysis area is 50.0 \(\mu\)m \(\times\) 50.0 \(\mu\)m, and the bright colors on the TOF-SIMS images correspond to the higher intensities of each species. We can clearly observe that both of these elements are distributed homogeneously in bimetal dendrite shapes. The X-ray diffraction (XRD) patterns, obtained for Zn, Au, and AuZn dendrites [[a–c] respectively in Fig. 1(D)], contain typical Au and Zn dendrite peaks at 2\(\theta\) values of 38°, 44°, 64°, and 77°; and 36°, 39°, 43°, 54°, 70°, 71°, and 78°, respectively. The XRD pattern of the AuZn dendrite [c] in Fig. 1(D)] contains high intensity peaks associated with both metals. Au and Zn are both homogeneously dispersed among each other. Overall, the homogeneous distribution of Au and Zn in the porous bimetal dendrites are expected to promote catalytic oxidation of glucose and reduction of \(\text{O}_2\). Compared to the corresponding pure Au dendrite, the Au peaks in the XRD pattern of the bimetal are slightly shifted and broadened. The index peaks, assigned as (111), (200), (220), and (311), identify the material as face-centred cubic (fcc) and appear at diffraction angles corresponding to electrodeposited fcc Au and Zn, respectively.

The catalytic characteristics were compared for both the oxygen reduction reaction (ORR) and glucose oxidation reactions, where the bimetal components were chosen due to the similar preparation conditions and catalytic properties of the FC reactions. The electrocatalytic activity of all the as-prepared materials towards the ORR was investigated in \(\text{O}_2\) and \(\text{N}_2\) saturated solutions. As shown in ESI† Fig. S1, the onset potentials of \(\text{O}_2\) in linear sweep voltammograms (LSVs) are \(-87.5\text{ mV for Pt}, \sim -66.4\text{ mV for Au dendrite}, \sim -47.7\text{ mV for AuZn dendrite}, \sim -48.9\text{ mV for AuNi dendrite, and \(-59.6\text{ mV for AuCo dendrite electrodes}}.\) The AuZn dendrite revealed the best performance compared with the other Au-transition-metal bimetals, so its FC reactions were extensively studied in the subsequent experiments. To elucidate the kinetic characteristics of the ORR, hydrodynamic voltammograms (HVs) using a rotating disk electrode (RDE) were collected for the \(\text{O}_2\) reduction process in a saturated 0.1 M NaOH solution [Fig. 2(A) and (B)]. For instance, the onset potential of the AuZn dendrite electrode shifts positively to +85.1 mV, and the diffusion current at \(-700.0 \text{ mV vs. } \sim 1.3 \text{ times larger than that of the Au dendrite electrode (with the onset potential shifted by } +38.2 \text{ mV}].\) The number of transferred electrons (n) per \(\text{O}_2\) molecule involved in the ORR was determined by using the Koutecky–Levich equation [eqn (1) and (2)] (see ESI†).\(^\dagger\) The n values, which are dependent on the potential, were observed to be 3.5, 2.6, 3.9, 3.5, and 3.1 for pure Pt, Au, AuZn, AuNi, and AuCo dendrite electrodes at \(- \sim 500.0 \text{ mV, respectively [inset of Fig. 2(A)]. The results demonstrate that the electrocatalytic activity of the AuZn dendrite towards the ORR is somewhat higher than those of metal and bimetal dendrites in terms of the onset and half-wave potentials. The number of electrons (n value) for the ORR at the AuZn bimetal dendrite electrode was observed to be always higher than those at the pure Au dendrite and pure Pt electrodes over the potential range that was probed. This observation indicates that the AuZn bimetal dendrite structure is a more efficient electrocatalyst for the ORR than the pure Au electrode, and its ORR process proceeds via a four-electron transfer pathway.\(^\dagger\) The Koutecky–Levich plot that was obtained to determine the kinetic proficiency of the test electrode displayed good linearity, with the slope remaining approximately constant over the entire potential range used. This might be related to the oxidation of Au(OH)\(_4\) (formed on the Au surface in the alkaline electrolyte) to a higher-valence oxohydroxide. HVs were collected using a RDE at various rotation speeds to gain further insight into the ORR performance of the AuZn.
dendrite [Fig. 2(B)]. The voltammograms show that in contrast to the bare Pt and Au dendrite electrodes, the AuZn dendrite deposited in the disk electrode region facilitates interaction with the electrolyte. At all rotation speeds, the limiting currents for the ORR at the AuZn dendrite electrode were higher than those for the ORR at the bare Pt and Au dendrite electrodes (not shown). In addition, the RDE experiment for the ORR was performed in a physiological pH medium (pH 7.4, containing 0.14 M Cl\(^{-}\)), 25 °C. As shown in ESI† Fig. S2, an increasing current density was observed with increasing rotation rates similar to that in an alkaline solution.

Cyclic voltammograms (CVs) of AuZn and (inset) Au dendrites in blank (black) and 10.0 mM glucose-containing (C) NaOH and (D) physiological conditions (pH 7.4, containing 0.14 M Cl\(^{-}\), 37.5 °C) (red) are displayed in Fig. 2. CVs for other electrode materials are shown in ESI† Fig. S3: (A) bare glassy carbon (GC), (B) bare Au, (C) AuNi, and (D) AuCo dendrite electrodes. CVs recorded for the Au dendrite exhibit redox peaks at +337.3/+107.3 and −225.9/−305.4 mV.\(^{18}\) A set of redox peaks for the AuZn dendrite additionally appears at −686.4/−754.1 mV, which correspond to redox processes of Zn. The redox peaks corresponding to the Au redox process of the AuZn dendrite appear at +551.3/+111.7 and −491.9/−611.2 mV, where the latter pair is a consequence of the oxidation of glucose to gluconolactone and other minor products (Fig. 2(C)). Otherwise, CVs recorded for the Au dendrite under physiological conditions exhibit a set of redox peaks at +265.8/+193.1 mV and an oxidation peak at +452.4 mV. On the other hand, two pairs of redox peaks for the polymer (Nafion/polyurethane) coated on the AuZn dendrite appear at −350.2/−533.7 and +173.0/+3.6 mV, where the former is responsible for a redox process of Zn, and the latter is for Au in a blank buffer solution as shown in Fig. 2(D). The dissolution of Zn ions from the polymer/AuZn surface was confirmed using EDXS, there is no dissolution of Zn under the physiological conditions (0.4% Zn was dissolved, which is within the experiment error range), while most of the Zn is dissolved from the AuZn surface in the acidic medium (98.8% Zn was dissolved).

The number of electrons involved in the glucose oxidation reaction at the AuZn bimetal electrode was determined by employing controlled potential coulometry, and the oxidation products were analyzed using high-performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESI MS) (see ESI† Fig. S4). The coulometric experiment was performed in a 5.0 mL blank solution (0.1 M NaOH) and separately in the same solution containing 1.0 μM glucose. The potential of +400.0 mV was applied for the glucose oxidation over 150 min. In both cases, charges (Q) of −24.4 and −3.31 mC for 120 min were obtained, respectively. The anodic products of glucose oxidation at the AuZn dendrite electrode were shown to be gluconolactone, amounting to 41% (2-electron oxidation product, EOP), with other minor products such as oxalate (15%, 18-EOP), formate (3%, 12-EOP), glyoxylate (8%, 12-EOP), glycolate (1%, 6-EOP), glucolate (25%, 6-EOP), 2-keto-gluconate (6%, 4-EOP), and glyceraldehyde (1%, 4-EOP).

Surface analysis of the dendrite was carried out using X-ray photoelectron spectroscopy (XPS) to confirm the composition and oxidation states of the AuZn bimetal. The XPS spectra displayed in Fig. S5 contain corresponding peaks of the dendrite associated with (A) the survey spectrum, (B) Zn 2p, and (C) Au 4f. The pristine dendrite (I) displays peaks at 1021.2 eV and at 88.2 and 84.3 eV, corresponding to Zn and Au, respectively,\(^{19}\) which indicates that both Zn and Au exist in their reduced metallic states. During the glucose oxidation and O\(_2\) reduction reactions, new XPS peaks appear at approximately 1022.2 eV and at 89.5 and 85.5 eV, which correspond to the respective peaks of ZnO and Au\(_2\)O\(_3\). As can be seen in (III) and (IV), the peak intensities corresponding to ZnO and Au\(_2\)O\(_3\) increase as the glucose oxidation and O\(_2\) reduction reactions continue, in contrast to the behaviour of the blank solution (II and IV).

Representative applications of the AuZn dendrite in a FC and a biosensor were demonstrated for standard glucose and blood samples. Fig. S6(A) (ESI†) shows a schematic representation of a GOFC composed of a pair of AuZn electrodes separated by a gap of 100 μm using a paper. The cell is composed of two compartments in which an O\(_2\) and a glucose-containing solution are externally connected in a closed loop with a FC system, which was operated at an open-circuit voltage. Fig. S6(B) (ESI†) shows the cell voltage and power density versus current density curves for the cell. The performance of the cell containing 100.0 mM glucose at 25 °C revealed the following characteristics: cell voltage of 0.91 V, current density of 2.83 mA cm\(^{-2}\), and power density of 1.63 mW cm\(^{-2}\). Besides glucose, human whole blood (blood glucose level of 108.5 mg dL\(^{-1}\), 25 °C) and 5.0 mM test glucose solutions (25 and 37.5 °C) were used as the anodic fuel. In this case, the cell performance had the following characteristics: cell voltage of 0.59, 0.62, and 0.63 V, current density of 1.21, 1.45, and 1.50 mA cm\(^{-2}\), and power density of 0.29, 0.38, and 0.41 mW cm\(^{-2}\). The power density obtained using a glucose test solution was 11.4 times higher than the previously reported one using a nonenzymatic-catalyst-based glucose–O\(_2\) system.\(^{20}\) This might be because a total number of 18 ± 1.5 electrons are involved in the glucose oxidation reaction at AuZn. The cell voltage and power density curves as functions of the temperatures (20–75 °C) and the glucose concentrations (500.0 nM–150.0 mM) were obtained in an alkaline solution (0.1 M NaOH), where the maximum power density
was 2.07 mW cm^{-2} at 50 °C (see ESI† Fig. S7(A and B) and Table S1). In addition, in vitro control experiments were performed under physiological conditions (pH 7.4, containing 0.14 M Cl\textsuperscript{-} and 37.5 °C) with the glucose concentrations between 0.01 and 50.0 mM. In this case, the power density was 0.41 mW cm\textsuperscript{-2} at 5.0 mM glucose (RSD (n = 3) was <7.3%) (see ESI† Fig. S7(C and D) and Table S1).

The current is proportional to the glucose concentration, which is potentially applicable for continuous in vitro glucose sensing. The maximum cell voltage, current density, and power density at a glucose concentration of 100.0 mM and at 50 °C are 0.98 V, 3.50 mA cm\textsuperscript{-2}, and 2.07 mW cm\textsuperscript{-2}, respectively. Long-term stability testing of a FC containing the dual AuZn dendrite electrodes was carried out for over 832 h, where the power density slowly decreased to a loss of 28.9% after 711 h of operation.

The performance of micro GC (cell size: 8 mm × 4 mm, diameter: 5.0 mm) and micro film (cell size: 4 mm × 6 mm, thickness: 1 mm, diameter: 3.0 mm) was measured in Wistar rats, which was evaluated using a pair of two carbon screen-printed micro film electrode (SPME) and GC. A biocompatible FC with a bimetal on the GC was implanted in the (ESI† Fig. S8(A)) abdominal cavity, and FCS with the micro film electrodes were implanted in (a) the subcutaneous layer of the neck, and (b) brain of a rat, separately (Fig. 3(A)), respectively. The implanted FC measured the power density while the rat was held in position on a stereotaxic frame and ORR processes were observed on the AuZn dendrite; the performance of the FC was much higher than that of pure Au or Pt electrodes. Importantly, the results show that electricity can be successfully generated from both the glucose–O\textsubscript{2} (2.07 mW cm\textsuperscript{-2} at 50 °C) and the whole blood–O\textsubscript{2} fuel systems using the AuZn dendrite. The micro film FC implanted in the rat brain remained stable for more than 18 days. In addition, the current of the FC is directly proportional to the glucose concentration, which is potentially applicable for a continuous in vivo glucose sensing.

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Notes and references