A new type of high performance air-breathing glucose membraneless microfluidic fuel cell

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ABSTRACT

Glucose membraneless microfluidic fuel cells have shown low cell performance with low oxygen mass transfer being one of the principal limitations. Herein, we report and discuss using air as an oxygen source to reduce the limitations of the cathode. The result was the first inorganic-catalyst air-breathing glucose microfluidic fuel cell, which shows the highest cell performance reported to date for this type of device: 1.6 mW cm^{-2} with a cell voltage and maximum current density of 0.83 V and 9.5 mA cm^{-2}, respectively. This record performance was attributed to the enhancement of the oxygen concentration, oxygen diffusivity and the metal–metal and metal-support interactions of the AuAg supported on multi-walled carbon nanotubes (AuAg/MWCNT) employed as electrocatalyst in the anode with 20% less Au-loading than Au/MWCNT material as comparison.

Introduction

Microfluidic fuel cells (MFCs) are electrochemical systems which convert chemical to electrical energy. In MFCs, fuel and oxidant are confined at microscale channels exhibiting some advantages such as: easiness to use liquid fuels, portability and higher surface area-to-volume ratio which enhance both thermal dissipation and electrochemical kinetics [1]. Also, due to micro-confinement, new phenomena occurs allowing to overcome some typical fuels cells problems: low Reynolds number (<10) are obtained indicating that streams are driven at a co-laminar flow; because of this, the use of a physical barrier such as a polymer ionic exchange membrane is avoided as well as its inherent problems [2]. Furthermore,

oncoming of electrodes not only could decrease ohmic losses but also could enhance reaction kinetic due to the bulk solution is closer to electrodes [3].

Glucose is a highly available, non-toxic and non-expensive industrial product. It shows a theoretical energy density of 4430 Wh kg^{-1}, a thermodynamic electro-oxidation potential of −0.69 V vs. SHE in alkaline media and a thermodynamic cell voltage of 1.09 V (using oxygen as oxidant). Interesting literature concerning glucose electro-oxidation oxidation and its mechanism can be found elsewhere [4,5,6]. Nowadays, it is known that gold and gold-based bimetallic materials are the best electrocatalysts toward this reaction, this can be attributed to the higher tolerance of gold to the poisoning effect of the adsorbed reaction intermediates compared with platinum-based materials [7,8,9]. Multiple methods have been

employed toward obtaining Au and Au-based nanoparticles: traditional chemical reduction method [10], sol-gel [11], micelles [12], reverse micelles [13], water-in-oil microemulsions [14] and through a seed solution [15].

The water-in-oil (w/o) microemulsion is one of the most common methods due to its advantages, such as its soft chemistry basis, it is easy to perform, easiness to obtain particle sizes between 5 and 50 nm, and does not demand extreme pressures or temperature control. Furthermore, w/o microemulsions are generally transparent, they are isotropic liquid media with nano-sized water droplets dispersed in a continuous oil phase. The water droplets can be stabilized by surfactant molecules at the water/oil interface offering a unique microenvironment for nanoparticle formation [16,17,18,19]. On the other hand, reverse micelles is the term related to the water-in-oil micellar aggregates which contains enough solutes — usually water — to form a well-defined fluid, offering easiness to obtain small nanoparticles, to control the particle size and to achieve a highly stabilized colloidal suspension [20]. Also, the nanoparticle size and its stabilization is strongly influenced by the micellar water pool size and the shell of surfactant molecules [13]. Different electrocatalysts such as AuNi [21], Ni [22], Pt_3Cu [23] and Pt–Ru–Ni [24], have been synthesized through this method. An extensive analysis of the effect of the chemical method on particle size/shape can be found elsewhere [25,26,27].

The use of gold-based materials as anodic electrocatalysts in abiotic glucose microfluidic fuel cells has been barely reported, where, in their totality, corresponded to works reported by our group. The synthesis and utilization of a specific Au and Au-based material was strongly influence by the cell design. For instance, in an MFC with "Y" shape in which electrodes were located at the microchannel walls, the anodic/cathodic stream flows over walls, consequently the limited geometric area and crossover effects were crucial to choose/synthesize a specific electrocatalyst. Also, in our group, three strategies have been followed in order to overcome these problems: I) using supports with high surface area such as carbon nanotubes (MWCNTs) [28] and polyaniline [29]. II) Enhancing the electronic properties by using bimetallic mixtures such as AuAg [30], PtAg [31] and AuPd [32]. III) Synthesizing Au with preferential (200) crystallographic planes to improve mass activity [33]. The following results were achieved using a "Y" shaped MMFC with electrodes located at cell walls: Au/MWCNTs showed a similar cell performance than Au/C (Vulcan carbon as support) ~0.28 mW cm^{-2} and a voltage of 0.7 V; however the gold mass content was 1.6 times lower in Au/MWCNTs [28]. The glucose electro-oxidation using Au/polyaniline was shifted 140 mV (−0.41 V vs. NHE) compared with Au/C, resulting in a cell performance of 0.18 mW cm^{-2} and a voltage of 0.5 V [29]. The use of AuAg produced a more negative oxidation potential than Au nanoparticles: −0.38 and −0.225 V vs. NHE, respectively. The cell performance was of ~0.3 mW cm^{-2} and normalized by gold content result in a 4-fold higher value than Au nanoparticles [30]. PtAg electrocatalyst showed high tolerance toward glucose oxidation exhibiting higher cell performance than Pt nanoparticles (Au/C as anode, 0.63 mW cm^{-2}) attributed to the decrease of crossover effects [31]. After this, AuAg [30] and PtAg [31] were used as the anode and the cathode respectively, achieving a power

density of 630 μW cm^{-2} at zero flow [34]. In a further MMFC, electrodes were placed on the cell floor in order to decrease crossover effects and to increase geometrical area. In this cell, AuPd with different mass content was synthesized by electrodeposition, where a ratio of $Au_{60}Pd_{40}$ resulted in the more negative potential toward glucose electro-oxidation (−0.41 V vs. NHE). This gold-palladium composition was used in an MMFC obtaining a power density of ~0.28 mW cm^{-2} [32]. Finally, Au with high amount of (200) terraces was also electro-synthesized in this cell design. This electrocatalyst showed high affinity toward glucose oxidation instead by-products (oxidation potential: −0.40 V vs. NHE). Also, a power density of 0.085 mW cm^{-2} was achieved at zero flow [33].

It has been observed a poor cell performance in those glucose membraneless microfluidic fuel cells compared to other types of micro fuel cells made using microtechnology, e.g. hydrogen [35,36,37] and methanol [38,39,40]. Glucose MMFCs shown limited power density — in the tens to hundreds of μW cm^{-2} range — whereas hydrogen and methanol micro fuel cells can produce more than tens to hundreds of mW cm^{-2}. Membraneless microfluidic fuel cells employ dissolved oxygen as an oxidant, exhibiting poor power density independently of the fuel used due to mass transfer limitations at the cathode, such as low diffusivity (2×10^{-5} cm^2 s^{-1}) and low oxygen concentration in aqueous media (2–4 mM) [41,42]. Therefore, air can be used in microfluidic fuel cells due to its higher diffusivity (10,000-fold) and higher oxygen concentration (10 mM) [42]. In the present contribution, AuAg and Au-based materials were synthesized by a reverse micellar method and supported on multi-walled carbon nanotubes (MWCNTs) to obtain small and well-dispersed nanoparticles in order to improve mass activity. The electrocatalytic properties of the mono- and bimetallic electrocatalysts were tested towards the glucose electro-oxidation reaction. These materials were then evaluated for the first time in a glucose membraneless microfluidic fuel cell which employs oxygen from air to enhance both diffusivity and oxygen concentration.

Experimental

Synthesis of catalysts

The synthesis of MWCNTs by spray pyrolysis was previously reported [43]. This material was used as a support during the catalysts preparation. Prior to use, the MWCNTs were treated with 9 M HNO$_3$ and refluxed at 120 °C for 24 h. They were then washed with distilled water several times and dried at 110 °C overnight. The reaction medium was integrated by the partially ionic w/o microemulsion, composed of Triton X-100 (Sigma−Aldrich, Laboratory grade) as a non-ionic surfactant and 2-ethyl-1-hexanol (Aldrich, ≥99.6%) as an ionic co-surfactant; these agents were dissolved in hexane (Sigma−Aldrich, 95%) as the oleic phase. The water/surfactant molar ratio was 3.5:1.

Au/MWCNT and AuAg/MWCNT catalysts were prepared using AgNO$_3$ (J. T. Baker, ≥99.0%) and HAuCl$_4$·3H$_2$O (Aldrich, ≥99.9%) as metallic precursor agents. A weight ratio of 80:20 gold-silver precursors were utilized to synthesize the AuAg/MWCNT electrocatalyst. Furthermore, the electrocatalysts