



Electrodeposited gold nanoparticles on carbon nanotube-textile: Anode material for glucose alkaline fuel cells

Mauro Pasta, Liangbing Hu, Fabio La Mantia, Yi Cui*

Department of Materials Science and Engineering, Stanford University, 94305 Stanford, CA, USA

ARTICLE INFO

Article history:

Received 25 February 2012

Received in revised form 6 March 2012

Accepted 12 March 2012

Available online 21 March 2012

Keywords:

Glucose electrooxidation

Conductive textiles

Gold electrocatalysis

Glucose fuel cell

ABSTRACT

In the present paper we propose a new anode material for glucose–gluconate direct oxidation fuel cells prepared by electrodepositing gold nanoparticles onto a conductive textile made by conformally coating single walled carbon nanotubes (SWNT) on a polyester textile substrate. The electrodeposition conditions were optimized in order to achieve a uniform distribution of gold nanoparticles in the 3D porous structure of the textile. On the basis of previously reported studies, the reaction conditions (pH, electrolyte composition and glucose concentration) were tuned in order to achieve the highest oxidation rate, selectively oxidizing glucose to gluconate. The electrochemical characterization was carried out by means of cyclic voltammetry.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The direct oxidation of glucose to produce electrical energy has been widely investigated because of renewability, abundance, high energy density and easy handling of the carbohydrate. Most of the earlier studies have been conducted in extreme conditions in order to achieve glucose complete oxidation to CO₂, neglecting the carbohydrate chemical instability that generally leads to useless by-product mixtures [1]. The partial oxidation to gluconate, originally studied for implantable fuel cells, has the advantage of generating a commercially valuable chemical [2].

In a previous study we characterized a commercial platinum based anode material, optimizing the operating conditions in order to selectively oxidize glucose to gluconate under alkali conditions, maximizing the current output [3]. The aim was also to produce an actual benchmark for the evaluation of new electrode materials. In this sense, gold has been demonstrated to be more active than platinum towards glucose electrooxidation in an alkali environment [4]. In order to improve our knowledge of the system, we first studied the mechanism of glucose electrooxidation at gold electrodes [5] and outlined the outstanding electrocatalytic properties of gold nanoparticles [6].

On the basis of these studies, here we propose a new anode material based on gold nanoparticles electrodeposited on conductive textiles prepared by conformally coating SWNT on a polyester matrix [7,8]. The tridimensional macroporous structure of the textile

backbone accounts for both higher metal mass loading per geometrical surface area and easier substrate diffusion while the microporosity of the CNT layer improves gold adhesion.

2. Experimental section

Sodium dodecylbenzene sulfonate (SDBS), sodium fluoride (99%, Alfa Aesar), D-(+)-dextrose (Sigma Aldrich), sodium phosphate dibasic anhydrous (99%, EMD), and gold (III) chloride trihydrate (99.9+%) were purchased from Sigma Aldrich. Nitric acid (68%) and glacial acetic acid were purchased from EMD Chemicals. Fluffy polyester sheets (Texwipe TX309) were purchased from Wal-Mart Inc.

Electrochemical characterization was carried out using a BioLogic VMP3 potentiostat–galvanostat multichannel equipped with an electrochemical impedance spectroscopy (EIS) board. A double junction Ag|AgCl|KCl (3.5 M) reference electrode (RE) was used in the measurement. The double junction was employed to prevent OH[−] diffusion and reaction at the Ag|AgCl interface. In addition, the RE potential was monitored after each measurement to confirm that no change had taken place. All the measurements were performed under inert (nitrogen) atmosphere and at room temperature.

2.1. Conductive textile fabrication

Conductive textiles are produced by a simple dip and dry process of a SWNT ink on a fluffy polyester textile. We refer to our previous paper [8] for a detailed description of preparation procedure and physicochemical characterization of the material.

* Corresponding author.

E-mail address: yicui@stanford.edu (Y. Cui).

2.1.1. SWNT ink fabrication [7]

10 mg/mL SDBS surfactant was dissolved in DI water with the help of bath sonication. Then, laser ablation SWNTs were dispersed in the surfactant solution to a concentration of 1.6 mg/mL. After bath sonication for 5 min, the CNT dispersion was probe-sonicated for 30 min at 200 W (VC 505, Sonics Inc.).

2.1.2. SWNT-textile preparation procedure [7]

A fluffy polyester sheet with thickness of ~1 mm is dipped into the SWNT ink and immediately removed. Due to the strong absorption, the ink quickly coats the textile. The textile with SWNT ink is subsequently dried in oven at 120 °C for 10 min to remove the water. The mass of the SWNT is obtained by the weight difference before and after the soaking of the cotton sheet. In this case, the process is repeated three times since we found out that it is the best compromise between sheet resistance of the textile ($<1 \Omega/\square$) and amount of SWNT employed (2.5 mg cm^{-2}) [8]. SEM images of the as prepared textile Fig. 2b reveal the macroporous structure of the textile sheet and Fig. 2c the conformal coating of SWNTs onto the fibers. This conformal coating is the result of the mechanical flexibility of the individual SWNTs and the strong binding energy between SWNTs and polyester fibers [9], accounting also for the high electrical conductivity of the textile. Previous studies have shown that SWNT films have micro scale porosity [10]; the microporous structure on top of the macroporous textile leads to what we call a “double porous structure”: the micropores facilitate the adhesion of the gold nanoparticles while the macroporosity facilitates the easy access of the reactant.

2.2. Surface modification

2.2.1. Surfactant removal

The material as prepared is highly hydrophilic, due to the SDBS still present on the surface. However this surfactant needs to be removed in order to avoid side reactions. Washing with abundant DI water and pressing with a grid is sufficient to remove the surfactant. The procedure is deeply described in [8].

2.2.2. SWNT-textile pretreatment

After the SDBS removal the textile exhibits a hydrophobic behavior that would be incompatible with its application in water-based electrolytes. To improve the surface hydrophilicity and remove the last traces of surfactant the textile is dipped into a 4 M HNO_3 solution for about 2 h, washed with DI water, dipped in glacial acetic acid for 2 more hours and washed again with DI water in order to completely remove the acid. Treating the nanotubes with nitric acid and glacial acetic acid introduces a larger number of oxygen-containing functional groups such as carboxyl, lactones and phenols and creates a more hydrophilic surface structure [11]. The nitric acid treatment also has two other advantages: it helps to remove impurities, such as catalytic metal particles responsible for self discharge problems [12] and induces hole doping, which decreases the resistivity of the nanotubes [13,14]. Fig. 1(a) shows the wettability test of the substrate after the acid treatment. As previously mentioned, the acid wash is also the final step in the surfactant removal process.

3. Results and discussion

A 1×1 cm of treated textile was dipped in the solution acting as working electrode (WE) while a platinum gauze was used as counter electrode (CE) in the presence of a Ag|AgCl|KCl 3.5 M reference electrode (RE). A 20 mM solution of AuCl_3 was employed as the gold precursor in the presence of a 0.6 M HCl supporting electrolyte. The electrodeposition was carried out with a chronoamperometry technique, fixing the potential at -0.6 V vs. RE, limiting the charge at 2 C. At sufficiently short times i.e. (before the overlap of diffusion layers), instantaneous nucleation results in a relatively narrow

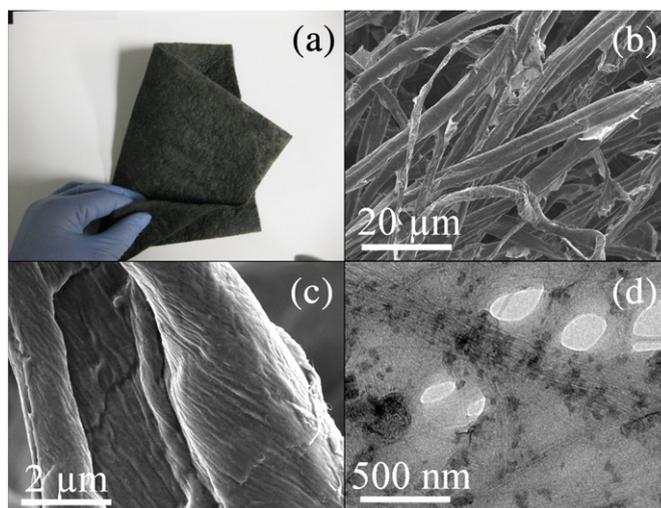


Fig. 1. (a) A $15 \text{ cm} \times 15 \text{ cm}$ foldable textile conductor based on a polyester sheet with sheet resistance of $2 \Omega/\square$. (b) SEM image of the cotton sheet coated with SWNTs. (c) Higher magnification image of the sample in (b) showing the conformal coating of SWCNTs on the cotton surface. (d) TEM image of SWNTs on a cotton fiber demonstrating that there is no evidence of agglomeration of SWNTs.

particle size distribution [15]. Progressive nucleation is observed when nucleation and particle growth coincide in time. As a result, the particle size distribution is broad [16]. At this potential, both gold deposition and hydrogen evolution take place; therefore, the coulombic efficiency is very low (around 15%, evaluated by dissolving in *aqua regia* the previously deposited gold and analyzing the final solution by ICP).

When dipped in aqueous solutions, the conductive textile tends to expand, having a thickness of about 0.5–1 mm. In order to optimize the current line distribution, a cell geometry with two platinum counter electrodes, each facing one side of the CNT/textile was employed. This results in a uniform particle distribution along the entire cross section of the textile as confirmed by Fig. 2a and b where SEM pictures of the exterior and interior parts of the material, respectively, are shown. The gold particles have a mean diameter of about 50 nm but they tend to aggregate (Fig. 2c). Their adhesion to the carbon nanotubes matrix is shown in Fig. 3d.

The performances of the Au-CNT/textile electrodes were tested by cyclic voltammetry using a 100 mM NaF, 100 mM buffer ($\text{NaH}_2\text{PO}_4/\text{NaH}_2\text{PO}_4$), pH 11.5 solution as the electrolyte and in the presence of 10 mM glucose as the substrate. Each component of the electrolyte

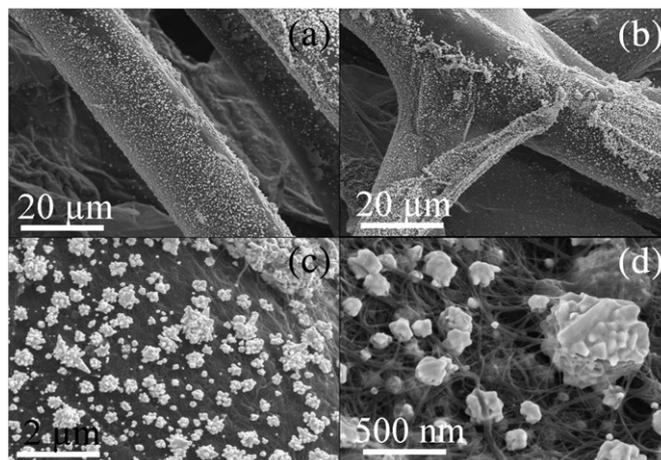


Fig. 2. SEM images of the (a) exterior and (b) interior of the CNT/textile after gold electrodeposition. (c, d) Higher magnification SEM images of the gold particles.

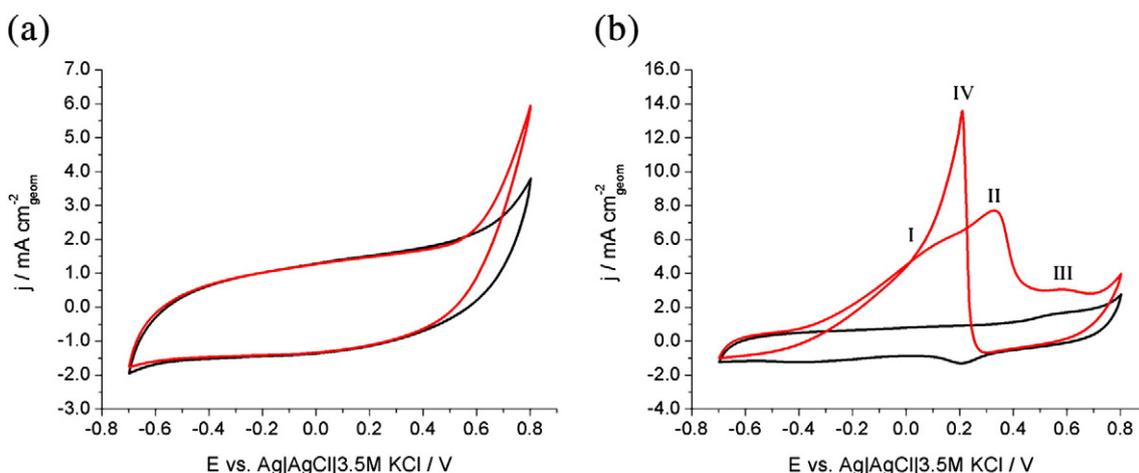


Fig. 3. Cyclic voltammograms of (a) plain CNT/textile and (b) Au-CNT/textile without (black curves) and with 10 mM glucose (red curves) in 100 mM K_2HPO_4/K_3PO_4 , 100 mM NaF electrolyte, pH 11.5. Scan rate of 20 mV s^{-1} . The current density is calculated on the basis of the geometrical surface area in contact with the solution. The capacitance of the textile substrate is 68 mF/cm^2 , 27 F/g of SWCNT.

has been especially designed on the basis of previous mechanistic studies [5]:

- pH 11.5: it is well known that glucose is unstable in aqueous solution and degrades into complex mixtures [17]. Nevertheless glucose electrooxidation is favored at high pH values [18]. 11.5 is the threshold pH value above which glucose is not chemically stable anymore in the operating conditions adopted.
- Buffer (NaH_2PO_4/NaH_2PO_4). The buffer has multiple effects on the process. The main function is to maintain a constant pH value near the gold surface while glucose is oxidized to gluconic acid. It also decreases the resistance of the solution. But, on the other hand, it gets adsorbed at the gold surface thus decreasing the active sites for glucose oxidation. At a 100 mM concentration the buffering effect is predominant.
- NaF. It is the supporting electrolyte. Among all the possible choices, it has the great advantage of not adsorbing at gold electrodes, thus not interfering with the first step of glucose electrooxidation, glucose oxidative adsorption [5].

Fig. 3a shows the cyclic voltammetry of the conductive textile before gold electrodeposition in both the presence and absence of glucose; as one can observe, the SWNTs are not active for glucose electrooxidation in the potential range investigated. In Fig. 3b in the absence of glucose we can see two electrochemical processes relative to gold hydroxide formation and reduction. The broad shape of the peak is due to the spatial distribution of gold particles along the entire cross section of the material. In the presence of glucose, the usual peaks of glucose electrooxidation at gold electrodes are present [5]. The glucose molecule is first electrochemically adsorbed at the surface of the electrode by dehydrogenation (peak I). The dehydrogenated molecule can be transformed to gluconate either by direct oxidation or through a δ -gluconolactone intermediate step, indistinguishable at room temperature (peak II). At higher potentials, the gold surface is oxidized to gold hydroxide (peak III), which is inactive towards glucose electrooxidation. During the cathodic scan, gold hydroxide is reduced, and therefore glucose can be re-adsorbed and oxidized, generating an oxidative peak in the cathodic scan (peak IV) used in a previous study to develop a new approach to glucose sensing [19].

From the charge underneath the peak relative to gold hydroxide formation (black curve in Fig. 3b), it is possible to estimate the real gold surface area [20] that in our case is in the order of 30 cm^2 per cm^2 of textile top-down area. Moreover, we know from previous studies [19] that the current intensity of the oxidative peak during the cathodic scan (Fig. 3b, peak IV) is proportional to the surface

area of gold effectively used to oxidize glucose to δ -gluconolactone. In our case, this value is around 20 cm^2 per cm^2 of textile geometrical area. The ratio between these two values gives an estimation of what we call effective area, which refers to the portion of the gold surface effectively employed. In our case about 2/3 of the electrodeposited gold is active, that, considering the thickness of the electrode is a promising result.

4. Conclusions

In the present paper, we proposed a new anode material for glucose–gluconate fuel cells prepared by electrodepositing gold nanoparticles onto a SWNT covered polyester substrate. The deposition conditions have been optimized in order to obtain a uniform distribution of gold nanoparticles along the entire cross section of the material. The 3D porous structure allows for efficient diffusion of the reactant inside the porous structure, demonstrated by the high gold efficiency while the microporosity of the CNT layer guarantees good electrical contact of gold nanoparticles and the current collector.

Acknowledgments

Y.C. acknowledges support from the King Abdullah University of Science and Technology (KAUST) Investigator Award (No. KUS-I1-001-12). The authors wish to thank James McDonough for his help in preparing the manuscript.

References

- [1] D.R. Wheeler, J. Nichols, D. Hansen, M. Andrus, S. Choi, G.D. Watt, *Journal of the Electrochemical Society* 156 (2009) B1201–B1207.
- [2] M. Comotti, C. Della Pina, M. Rossi, *Journal of Molecular Catalysis A: Chemical* 251 (2006) 89–92.
- [3] M. Pasta, F. La Mantia, R. Ruffo, F. Peri, C.D. Pina, C.M. Mari, *J. Power. Sources* 196 (2011) 1273–1278.
- [4] Y.B. Vasil'ev, O.A. Khazova, N.N. Nikolaeva, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 196 (1985) 127–144.
- [5] M. Pasta, F. La Mantia, Y. Cui, *Electrochimica Acta* 55 (2010) 5561–5568.
- [6] M. Pasta, R. Ruffo, E. Falletta, C.M. Mari, C. Della Pina, *Gold Bulletin* 43 (2010) 57–64.
- [7] L. Hu, M. Pasta, F. La Mantia, L. Cui, S. Jeong, H.D. Deshazer, J.W. Choi, S.M. Han, Y. Cui, *Nano Letters* 10 (2010) 708–714.
- [8] M. Pasta, F. La Mantia, L. Hu, H.D. Deshazer, Y. Cui, *Nano Research* 3 (2010) 452–458.
- [9] T. Hertel, R.E. Walkup, P. Avouris, *Physical Review B: Condensed Matter and Materials Physics* 58 (1998) 13870–13873.
- [10] D.S. Hecht, L. Hu, G. Grüner, *Current Applied Physics* 7 (2007) 60–63.
- [11] M. Lewin, E.M. Pearce (Eds.), *Handbook of Fiber Chemistry* Second Edition, 1998, Revised and Expanded. [In: *Int. Fiber Sci. Technol. Ser.*, 1998; 15].

- [12] K. Tohji, T. Goto, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga, Y. Nishina, *Nature* 383 (1996) 679.
- [13] B.B. Parekh, G. Fanchini, G. Eda, M. Chhowalla, *Applied Physics Letters* 90 (2007) 121913/121911–121913/121913.
- [14] E. Beaudrouet, A. Le Gal La Salle, D. Guyomard, *Electrochimica Acta* 54 (2009) 1240–1248.
- [15] T.S. Olson, R.A. Rincon, D.A. Brevnov, P. Atanassov, *Electrochemical and Solid-State Letters* 13 (2010) D11–D14.
- [16] R.M. Penner, *Journal of Physical Chemistry B* 106 (2002) 3339–3353.
- [17] B.Y. Yang, R. Montgomery, *Carbohydrate Research* 280 (1996) 27–45.
- [18] P. Schechner, E. Kroll, E. Bubiš, S. Chervinsky, E. Zussman, *Journal of the Electrochemical Society* 154 (2007) B942–B948.
- [19] M. Pasta, F. La Mantia, Y. Cui, *Electrochemistry Communications* 12 (2010) 1407–1410.
- [20] B. Lertanantawong, A.P. O'Mullane, W. Surareungchai, M. Somasundrum, L.D. Burke, A.M. Bond, *Langmuir* 24 (2008) 2856–2868.