FABRICATION AND CHARACTERIZATION OF HIGHLY MINIATURIZED AND BIO-COMPATIBLE ELECTROCHEMICAL CAPACITOR USING 3D HYBRID AU-/NPTS ELECTRODES AND NAFION SEPARATOR

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Abstract: A biocompatible and robust electrochemical capacitor (EC) based on highly catalytic 3D hybrid macroporous Au with Pt nanoparticles (macroporous Au-/nPts) electrodes was fabricated and characterized for highly miniaturized and implantable biofuel cells (BFCs) integrated with energy storage device applications. The fabricated hybrid electrodes and EC device were characterized in 0.1 M phosphate buffered saline (PBS) solution and exhibited extremely large capacitance of 111 mF/cm^2, average power density of 8.6 mW/cm^2, and robust stability by charge-discharge characteristics at ambient temperature and pressure.

Keywords: Biocompatible, Electrochemical capacitor, 3D hybrid, Au-Pt nanoparticles, Nafion

INTRODUCTION

Due to the environmental pollution crisis by fossil energy source combustion and increasing energy demands, the considerable attention for renewable and reproducible energy source has been focused as very important research issue. Especially, biofuel cells (BFCs) can be applied not only for the conversion of biomass, but also as alternative energy sources for future implantable bio-medical devices and systems, such as implantable glucose sensors in artificial pancreas [1]. However, there are inherent problems of very low single cell voltage. Thus, these BFCs are arranged in a parallel in order to increase the output power and also arranged in a series to obtain high output voltage. The BFC can also be connected to an electrochemical capacitor (EC) for increasing the voltage output. When the generated electricity from the BFC is charged in the EC, we can achieve enough power with high voltage and current to operate the bio-medical devices [2].

The EC or super-capacitor devices have been received considerable attention over the last decade years for using energy storage devices. The capacitance of EC can usually obtain from redox reactions of electroactive species on electrode materials or charge-discharge processes at the electrical double layer (interfacial layer between electrode and electrolyte). Aforementioned redox reaction based capacitance (pseudo-capacitance) should be required reversibly oxidized and reduced potential materials at various potential states. Therefore, various electrode materials, such as conducting polymers and transition metal oxides based on relatively high surface activation area, have been researched for highly performed pseudo-capacitors [3-5].

Meanwhile, novel metals such as Au and Pt are suitable catalysts for portable as well as in-vivo bio-medical devices because of their long-term stability and biocompatibility.

In this research, we have developed macroporous Au-/nPts 3D hybrid electrodes to apply for anode and cathode of EC which could be integrated with implantable BFCs. These two 3D hybrid electrodes were then sandwiched with Nafion film for fabricating a highly performed EC device. The fabricated EC device has been characterized and analyzed to verify its usefulness and applicability for implantable bio-medical devices and systems. Since the macroporous Au with Pt nanoparticles (macroporous Au-/nPts) 3D hybrid electrode has extremely enlarged surface activation area, high amounts of positive and negative ionic charges within capacitor electrolyte can be accumulated on the electrode surface resulting in high energy density. In addition, its excellent catalytic characteristic is highly effective to increase the redox reaction.

CHEMICALS

All chemicals used in this investigation were of analytical grade and without further purification. In all experiments, deionized water (>18 MΩ-cm) from pure water generation system was used. The aluminum sec-butoxide, stearic acid and magnesium stearate, $HAuCl_4$, acid etchant (mixture of 11.8 M H_3PO_4 and 0.6 M HNO_3), and $NaBH_4$ were prepared for preparing the macroporous Au electrode [6]. The electroplating solution for the Pt nanoparticles was prepared with $C_{16}EO_8$ (octaethylene glycol monohexadecyl ether, 98 % purity, Fluka), 29 % (w/w) deionized water (18 MΩ-cm) and 29 % (w/w) HCPA (hexachloroplatinic acid hydrate, 99.9 % purity, Aldrich) [7]. Nafion film with 25 μm in thickness was used as a separator between anode and cathode electrodes for realizing the proposed EC device. All electrochemical experiments were performed in 0.1 M phosphate buffered saline (PBS, pH 7.4).

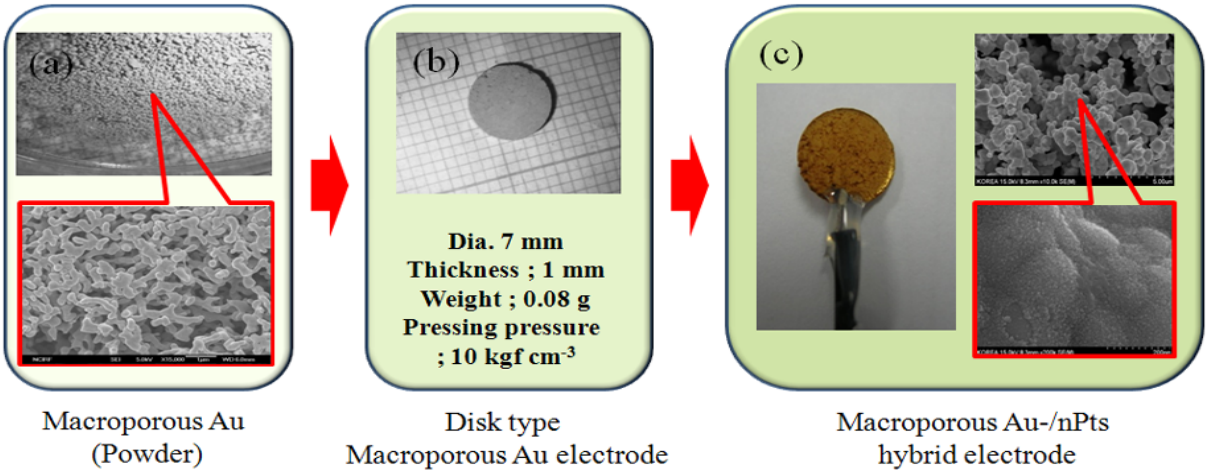

Fig. 1: Fabrication sequence of the macroporous Au-/nPts 3D hybrid electrode using the sol-gel process and electroplating technique energy harvesting from wave power.

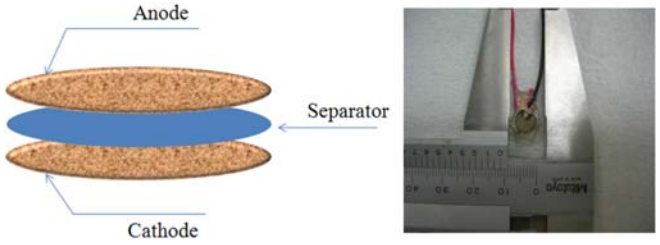

Fig. 2: Conceptual drawing and photograph image of the fabricated EC device.

The electrochemical characteristics of the fabricated hybrid electrodes were measured by using an electrochemical analyzer (Model 660D series, CH Instruments Inc., USA) at room temperature. A three electrode system was used, including the fabricated electrode as a working electrode, a flat platinum (Pt) bar as a counter electrode, and an Ag/AgCl reference electrode with 3 M NaCl. The impedance analysis was also carried out by using the electrochemical analyzer in the frequency regime ranged from 0.1 Hz to 50 kHz.

FABRICATION

Fig. 1 shows overall fabrication sequences for the proposed macroporous Au-/nPts 3D hybrid electrodes. The macroporous Au prepared by using the templating method and sol-gel process looks like a powder (Fig. 1(a)). The coral-like structured macroporous Au powder was comprised of aggregated Au particles. In the respective step, the surface morphologies for macroporous Au and hybrid electrode were investigated by FESEM. The detailed description for coral-like structured 3D macroporous Au electrode and hybrid electrode with Pt nanoparticles were depicted in our previous works [6]. Since the macroporous Au was finally formed as powder, the powders were mechanically pressed at room temperature into a circular mold (Dia. 7 mm) for making a disk-type electrode (Fig. 1(b)). After then, Pt nanoparticles were electroplated on the surface of the disk-type macroporous Au electrode for making highly

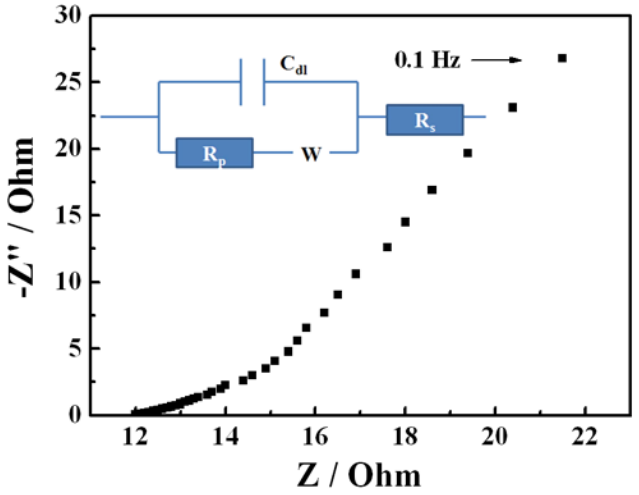

Fig. 3: Niquist plot for the fabricated 3D hybrid electrode in 0.1 M PBS (pH 7.4) containing 10mM $K_3Fe(CN)_6$ as redox probe.

roughened and catalytic hybrid electrode (Fig. 1(c)). The detailed electroplating method was also dealt in our previous work [6, 7].

The surface morphology analysis of the 3D hybrid electrode was performed by cracking the disk type electrode for checking how well deposited Pt nano-particles in inside pores of the macroporous Au. As shown in Fig. 1(c), Pt nanoparticles were very well distributed on the surface of the macroporous Au [6]. The fabricated 3D hybrid electrode was used as anode and cathode for the EC device, respectively.

Fig. 2 shows the conceptual drawing and photograph image of the fabricated EC device. The EC device is comprised two fabricated 3D hybrid electrodes with 7 mm diameter and 1 mm thickness, which was separated with a Nafion film by pressing at ambient temperature and pressure.

EXPERIMENTAL RESULTS

1. EIS analysis of the 3D hybrid electrode

Electrochemical impedance spectroscopy (EIS) can provide useful information to characterize

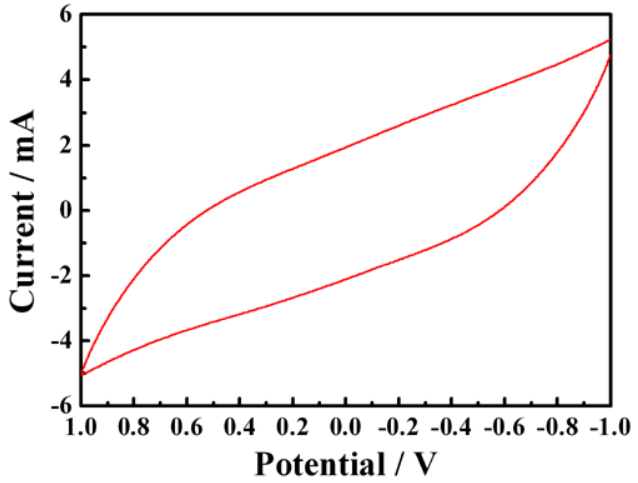

Fig. 4: Cyclic voltammetry curve of the fabricated EC in 0.1 M PBS solution (pH 7.4). The scan rate is 50 mV/sec.

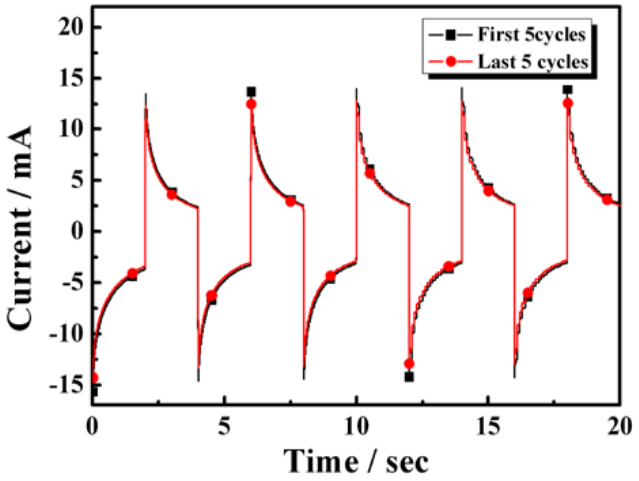

Fig. 5: Charge-discharge curves from 0 to 1V. The red curve presents the initial 5 cycles, the black one is another 5 cycles after more than 100 cycles.

interface properties of electrode surface. Fig. 3 shows the Nyquist impedance plot for 3D hybrid electrode using $Fe(CN)_6^{3-}$ as the redox probe. The imaginary part of impedance was plotted as a function of the real component in the frequency range from 0.1 Hz to 50 kHz. In order to fit impedance data, we selected Randle's circuit (upper right trace in Fig. 3). It is consisted of the ohmic resistance of the electrolyte (R_s), double-layer interfacial capacitance (C_{dl}) by the electrochemical charging-discharging process, electron transfer resistance (R_p) by the electron transfer kinetics of the redox probe at interface of the electrode, and Warburg impedance (W) representing the impedance of the diffusion processes [8, 9].

Generally, the relationship of R_p and C_{dl} at the high frequency region gives rise to a small semicircle due to diffusion effect of the electrolyte in the electrode [10]. As shown in Fig. 3, the EIS of the macroporous Au-/nPts 3D hybrid electrode shows an almost straight line at all frequencies, which can suggest that R_p for the electrochemical probe at the macroporous Au-/nPts electrode be almost zero [9]. This value is much smaller than that of the generally used plane Au electrode, indicating that electron transfer of the probe is faster at the macroporous Au-/nPts electrode than at the plane Au electrode.

2. Cyclic voltammetry of the 3D hybrid electrode

Cyclic voltammograms (CV) of the fabricated EC device with macroporous Au-/nPts 3D hybrid electrodes in 0.1 M PBS solution (pH 7.4) was recorded at the scan rate of 50 mV/sec, as shown in Fig. 4. The capacitance of the fabricated EC device can be calculated from the measured data by means of the relation (1):

$$\text{Capacitance: } C = \frac{I}{(dV/dt)} \qquad (1)$$

where I is the current of the CV curve and dV/dt is the scanning rate. As shown in Fig. 4, it exhibited the nearly rectangular shape resulting in an excellent capacitance property. At 0V, the capacitance is calculated to be 42.2 mF. As the effective area of the EC device is 0.38 cm^2, a specific capacitance (capacitance per unit area) density of 111 mF/cm^2 is deduced. This measured and calculated capacitance per unit area of this EC is obviously greater than that of the previous reported ones [11-13]. Although we use PBS solution as electrolytes for biocompatibility, the capacitance density was much enlarged. This result might be caused by extremely enlarged surface area according to the macroporous Au structure and well deposited Pt nanoparticles.

3. Charge-discharge characteristics

The charge-discharge characteristic of the EC device was measured in 0.1 M PBS (pH 7.4) solution by using a chronoamperometric test. As shown in Fig.5, the fabricated EC device is well charged and discharged between 0 and 1 V for more than 100 cycles. When the initial 5 cycles are compared with the last 5 cycles of curve shown in Fig. 5, it exhibits an excellent stability. Furthermore, the average power of self charge from this measured data was also evaluated by using the following formula (2):

$$\text{Average power: } \overline{P} = \frac{1}{T}\int_{t}^{t+T} VI\,dt \qquad (2)$$

where T is the charge time, V is the charge voltage, and I is the charge current measured on this amperograms. From the above equation and the measured curve, the average charge power was calculated as 27 mW (8.6 mW/cm^2) in half cycle.

CONCLUSIONS

A newly developed biocompatible and robust electrochemical capacitor based on macroporous Au

with Pt nanoparticles 3D hybrid electrodes has been fabricated and characterized. The coral-like structured macroporous Au and Pt nanoparticles were fabricated by using sol-gel process, templating method, and electroplating technique. A disk type hybrid electrode was then fabricated by pressing them into a jig at room temperature. For fabricating the EC device, two disk type electrodes (anode/cathode) were sandwiched with Nafion film as a separator. The fabricated 3D hybrid electrodes exhibited almost zero of electron transfer resistance by using EIS analysis. Enlarged surface area of 3D hybrid of the macroporous structure and Pt nanoparticles was highly effective to increase the capacitance of the electrochemical capacitor. The fabricated EC device exhibited fast charge rate and excellent stability between initial cycles and last cycles after 100 cycles. The relatively fast charge rate was caused by shorten ionic transfer length having low electron transfer resistance within the macroporous Au structure and highly catalytic characteristic of the enlarged surface area. These results indicated that the fabricated 3D hybrid electrode materials based electrochemical capacitor is suitable for integrating with implantable biofuel cell devices or systems.

ACKNOWLEDGMENTS

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