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Anodized stainless mesh for flexible battery anodes

D-T Nguyen¹, K Iwai¹, K Kawakami¹ and K Taguchi^{1*}

¹Department of Electrical and Electronic Engineering, Ritsumeikan University, 1-1-1, Noji-Higashi, Kusatsu, Shiga, Japan.

*Email: taguchi@se.ritsumei.ac.jp

Abstract. The fast development of flexible electronic devices in recent years requires the development of flexible batteries. In this study, a compact and flexible battery (15 mm \times 15 mm) was developed. The anode electrode of the battery was based on an anodized stainless mesh coated multiwalled carbon nanotubes (MWCNTs). The battery can be activated anytime, anywhere, by saline solution. The anodization process was applied to the anode electrode. After the heat-treatment process, the anodized stainless mesh was coated MWCNTs. The power generation characteristics of the flexible battery were investigated. Two types of anode electrodes made of stainless mesh with and without anodization were used for the experiment. The anodized stainless mesh anode generated 169 μ W/cm², which is four times higher than that of the anode without anodization, $4\overline{1.9} \mu W/cm^2$.

Keywords: Anodization, ammonium fluoride, ethylene glycol, stainless mesh, annealing.

1. Introduction

Recently, the intensive development of flexible electronic devices leading to the development of flexible materials used for developing flexible batteries [1]. Stainless mesh is a flexible material and can be used for fabricating battery electrodes. The stainless mesh also contains about 70 % of iron, which can be oxidized to obtain Fe_2O_3 , which is usually utilized to fabricate electrodes in batteries [1]. In saline solution (3.5%), the corrosion affects strongly on gray iron and steel [2]. The surface of the steel is protected by a thin film of iron oxide at room temperatures and dry air conditions. However, this thin protective layer has no effect when there is the presence of corrosive electrolytes [3].

One of the methods which can enhance the performance of the anode electrode in metal-based batteries is anodization [4]. In the anodization process, nanotubes of metal oxide grow on the surface of the anodized electrode [5]. With suitable conditions, the nanotubes reach a steady-state, which results in the creation of a layer of porous nanotube structure[4]. This anodization process enhanced the surface area of the anodized electrode [6].

In the previous study, a flexible battery that used heat-treated stainless mesh as the anode electrode was fabricated [7]. Besides, the anodized stainless mesh was coated with multiwalled carbon nanotubes (MWCNTs) [8, 9]. This paper focuses on enhancing the performance of the flexible battery by improving the performance of the anode electrode. Anodization method was applied to increase the surface area of the stainless mesh anode. The performance of the cells with the anodes with and without anodization was evaluated.

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2. Materials and methods

2.1. Anodized method

Fig. 1 shows the diagram of the experimental setup of anodization. A two-electrode electrochemical cell was used to conduct the anodization process. Platinum and stainless mesh were used as the cathode and anode, respectively. 30 V DC voltage was applied to the two electrodes. This cell used solution 1: 3.0g deionized water, 0.45g ammonium fluoride (NH₄F, Wako, Japan), and 56.35g Ethylene glycol (EG, Wako. Japan). The volume of the electrolytic solution was 60 ml. The distance between the stainless mesh and Pt electrodes was 2.5 cm. The anodization time was 10 min.



Figure 1. Anodization setup.

2.2. Battery design and electrode fabrication

Fig. 2 shows the battery structure. This battery composed of three main parts: an anode electrode, a membrane, and a cathode electrode. The anode electrode $(1 \text{ cm} \times 1 \text{ cm})$ were made of the anodized stainless mesh. After the anodization, the anodized stainless mesh was washed with purified water and dried at room temperature; after that, calcination was carried out at 500 °C for 30 min.

Moreover, the anodized stainless mesh dip-coated in MWCNT dispersion solution (N7006L, KJ Specialty Paper, Japan) for 1 min. MWCNT dispersion coating liquid was dispersed using an ultrasonic homogenizer for 20 min before dip-coating the electrode. Subsequently, annealing was carried out at 200 °C for 30 min. The MWCNTs coating enables good conductivity and maintains the flexibility of the anodized stainless mesh [10].

The cathode electrode (1cm \times 1cm) was made of hydrophilic carbon sheets coated potassium ferricyanide (Wako, Japan). Hydrophilic carbon sheet was dip-coated in a 0.75 M potassium ferricyanide solution for 1 min and dried at 60 °C for 20 min.



Figure 2. Structure diagram of the battery.

2.3. Measurement setup

The experimental setup is shown in Fig. 3. An external resistor was used to discharge the battery. The voltage between the anode and cathode was measured and recorded by a data acquisition system (DAQ, NI USB-6211). The current through the resistor was calculated using Ohm's law. To measure the power density curves, 80, 50, 12, 10, 5, 2, 1, 0.8, 0.5, 0.3, 0.1, 0.04 and 0.01 k Ω resistors were respectively connected to the external circuit to discharge the battery. The discharging voltage was recorded to calculate the power density



Figure 3. Experimental setup.

3. Results and discussions

3.1. Experimental reaction

After dropping the NaCl solution to the anode electrode to activate the battery, iron in the stainless mesh is oxidized to form Fe_2O_3 . The reaction is described in equation (1).

$$2Fe + 3H_20 \to Fe_2O_3 + 6H^+ + 6e^-$$
(1)

On the cathode side, potassium ferricyanide works as an electron acceptor. The reduction reaction of ferricyanide ions to ferrocyanide ions is described in equation (2).

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$$
 (2)

Ferrocyanide ions migrate from the cathode to the anode to react with Fe_2O_3 to form Prussian blue $(Fe_4[Fe(CN)_6]_3)$, which is generated based on equation (3), which shows the reaction between Fe_2O_3 and ferrocyanide ions $([Fe(CN)_6]^{4-})$, and this reaction enhances the output voltage.

$$2Fe_2O_3 + 6H_2O + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3 + 120H^- + 12e^-$$
(3)

3.2. SEM images

SEM was used to observe the surface of the anodized stainless mesh. Fig. 4 displays the SEM photo images of the stainless meshes without and with anodization. It can be seen that there were nanotubes formed on the surface. As a result, the surface area of the anodized stainless mesh is expected to increase significantly. The larger surface area is expected to contribute to the progress of generating electricity by the battery.

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Figure 4. SEM images of the stainless mesh without anodization (a) and the anodized stainless mesh (b).

3.3. Power density

The batteries using the anodes with and without anodization were measured. As shown in Fig. 5, the maximum power density of 169 μ W/cm² was achieved with the battery using the anodized stainless mesh anode at 100 Ω external resistance. Meanwhile, that of the battery using the anode without anodization was only 41.9 μ W/cm² at 800 Ω external resistance. Based on this result, It can be confirmed that extending the surface area of the anode by anodization method can enhance the power density of the battery.



Figure 5. The power density of the batteries using the anodes with and without anodization.

4. Conclusion

In this study, the performance of the flexible battery was enhanced by anodizing the stainless mesh anode. By conducting anodization, the surface area of the stainless mesh anode became larger. The enhancement of the surface area of the anodized stainless mesh was attributed to the formation of nanotubes on the surface, which was confirmed by SEM observation. The maximum power density of the battery using the stainless mesh anode with anodization (169 μ W/cm²) was four times higher than that of the battery using the stainless mesh anode without anodization (41.9 μ W/cm²). This result confirms the superior characteristics of the anodized stainless mesh anode fabricated by the method described in this study.

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