

Preparation of Cu foam by electrodeposition of Cu particles

Yuya Yato¹, Nur Farhana Binti Halid¹, Makoto Chiba¹, Mai Takase², Shigeaki Abe³,
Atsushi Hyono^{1*}

*1: National institute of Technology, Asahikawa College, 2-1-6 Shunkoudai 2jo, Asahikawa, Hokkaido, Japan

Fax: 81-166-55-8082, e-mail: hyono@asahikawa-nct.ac.jp

2: Muroran Institute of technology, 27-1 Mizumoto-cho, Hokkaido, 050-8585, Japan

3: Faculty of Dental Medicals and Engineering Graduate School of Dental Medicine, Hokkaido University, Kita 13, Nishi 7, Kita-ku, Sapporo, 060-8586, Japan

Copper porous structures for the substrates of the lithium battery electrodes were synthesized by the electrodeposition of copper particles. The relationship between the structures and the compositions of dispersion medium was investigated. Gelatin or hydrazine monohydrate was needed for the porous structures formation. Gelatin concentration affected the pores size in the structures. The higher gelatin concentration was, the smaller the pore diameter became. The surface energy of dispersion medium affected the size of hydrogen bubbles generated during the electrodeposition. It was suggested that by controlling the surface energy, it is possible to control the structure and pore size.

Key words: high surface area electrode, copper particles, electrodeposition

Introduction

Recently, the development of anode material in lithium batteries has been focused on. Tin is one of the candidates because of its high theoretical capacity. However, tin can expand during electrochemical reactions resulting to shorter life cycle. Do Hwan Nan et al. developed a three-dimensionally porous with large surface area by electrodeposition [1]. This Cu foam would be appropriate as a substrate for Sn electrodes. The structures of this Cu foam can be controlled by current density or various additives. They find the mechanical properties depended on shape of deposited Cu. In fact, the properties of Cu foam contained sphere-shaped particles was higher than that contained dendritic structures..

In this study, the preparation of 3-D Cu foam structure by the electrodeposition method of Cu particles was carried out. Compared with electroplating from ionic solution, this method can allow to prepare wide variation of the structures because Cu particles were synthesized as required shape.

Experimental

Cu particles synthesized was carried out according to Yonezawa's conditions [2]. The

particles were synthesized by the reduction of cupric sulfate pentahydrate. 5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 4.6 g of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ were dissolved into 100 mL of water and 250 g of gelatin was introduced into this solution. Then, 6 g of NaOH was added to adjust pH. After stirring for 30 min, 30 mL of 10 M aqueous $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution was added slowly introduced to the solution, which is kept stirred for 2 h at room temperature. The obtained particles were collected by filtration over a PTFE membrane filter (ADVANTEC, $1.0\ \mu\text{m}\phi$) and rinsed intensively with water.

Collected precipitates were redispersed in 100 mL of water containing 6 g of NaOH. Gelatin (0, 5, 50 or 250 mg) and/or 30 ml of 10 M aqueous $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ were added to the dispersion.

For preparation of electrode, Cu particles were deposited on a Cu plate in the dispersion with a constant voltage of 1, 3, and 5 V for 5 min. Cu plate was used as working electrode. Platinum plate was used as counter electrode. Distance between electrodes was 3 cm. The application period is 5 min.

Results and Discussion

The surface of Cu structure was observed by scanning electron microscopy (SEM, JEOL JSM-6510LA). These Cu foam structures were evaluated as electrochemical surface area by the cyclic voltammetry in 0.1 M KClO_4 aqueous solution deaerated with N_2 . $\text{Ag}/\text{AgCl}/\text{sat. KCl}$ aqueous was used as reference electrode. Potential scan range was $-1.2 \sim +0.3\ \text{V}$. Potential scan rate was $20\ \text{mVs}^{-1}$.

The SEM images of the structures foamed by electrodeposited Cu particles by 5 V for 5 minutes in the dispersion with (a) 1.5 M NaOH, (b) 1.5 M NaOH and 0.25 w/v% gelatin and (c) 1.5 M NaOH and 4.6 M hydrazine monohydrate were shown in Fig. 1. Without NaOH, Cu particles aggregated in the dispersion. The structure with no pore was observed when NaOH added only. (Fig. 1 (a)) These structures became black from original brown color. This suggested that the Cu particles were oxidized to cupric oxide. Under gelation or hydrazine monohydrate addition, the Cu particles kept original color. When gelatin was added, small pores under $10\ \mu\text{m}$ in diameter were observed. When hydrazine monohydrate was added, the structure with large pores was observed.

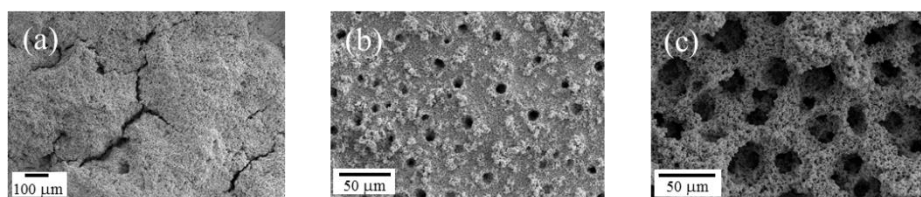


Fig. 1 SEM images of the structures by electrodeposition of Cu particles dispersion in different medium. (a) with NaOH only (b) NaOH and gelatin (c) NaOH and hydrazine monohydrate.

For clarifying the foaming process of porous structure, the dependence of the structures on the gelatin concentration and the voltage which was applied during the electrodeposition was investigated. The SEM images of the foam structures made under applied voltage, 1, 3 and 5V for 5 minutes in the dispersion with 0, 0.005, 0.05 and 0.25 w/v% gelatin concentration were shown in Fig. 2. As the voltage increased, the amount of deposited Cu particles increased. At 1V, corresponding to the initial stage of the structure growth, particles

was deposited as large blocks in low gelatin concentration. On the other hand, with the high gelatin concentration particles were deposited as small blocks. Over 3 V, the Cu particles were deposited over the whole surface. Large porous were observed on the surface of the samples deposited in the lower gelatin concentration, and much smaller porous were found on those in higher gelatin concentration.

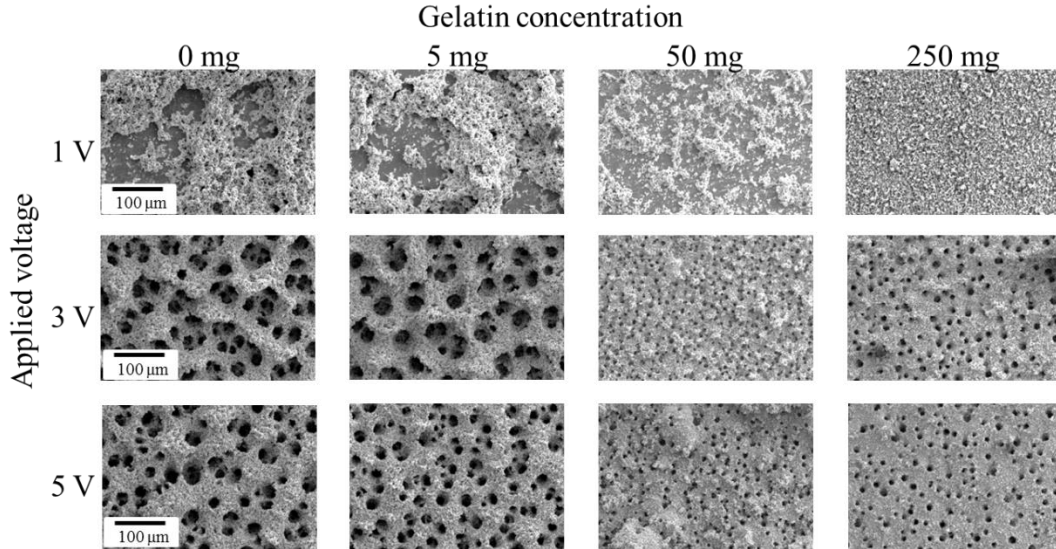


Fig. 2 SEM images of the porous structures electrodeposited under various condition, applied voltage, 1, 3 and 5 V, added gelatin concentration, 1, 5, 50 and 250 mg.

The dependences of porous area and the separate distance between porous on the gelatin solution were shown in Fig. 3. Fig. 3 (a) shows the schematic illustration of the radii of a porous; r , and the separation distance between neighboring porous; d . The surface area of porous; A were calculated with r . Both of the surface area (b) and the separation distance (c) were decreased as gelatin concentration increased, and a plateau values. It is suggested that these changes corresponds to that of the surface energy of the dispersion medium.

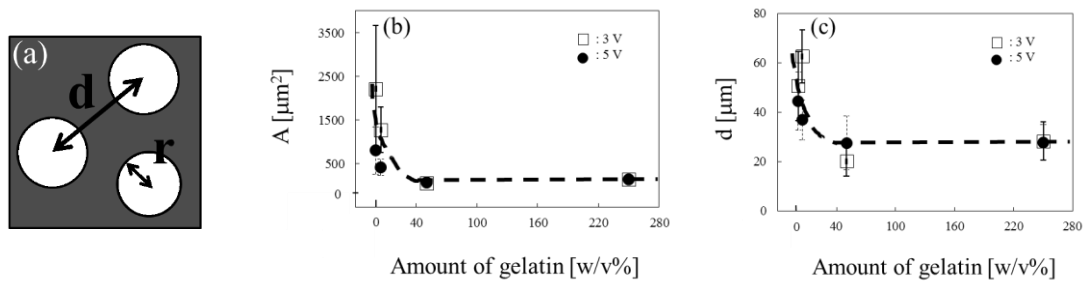


Fig. 3 Schematic illustration of the porous on the structures (a). The dependence of the area of pores (b) and the separation distance (c) on the gelation amount.

The tendency mentioned above is parallel to the study by Heon-Cheol et. al [3].

It was suggested that the manipulation of structure and pore size are possible by manipulating the surface

energy of the dispersion.

Reference

- [1] Do Hwan Nam, Ryoung Hee Kim, Dong Wook Han, Hyuk Sang Kwon, *Electrochimica Acta*, 66, 126 (2012)
- [2] Tetsu Yonezawa, Naoki Nishida, and Atsushi Hyono, *Chem. Lett.*, 39, 548 (2010)
- [3] Heon-Cheol Shin and Meilin Liu, *Chem. Mater.*, 16, 5460 (2004)