New preparation method of NiO electrode for super capacitor using aqueous electrolyte

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Introduction

Ni based electrodes are widely used as positive electrode for Ni-MH and Ni-Cd batteries. Previously, we applied NiO electrode to the positive electrode for hybrid capacitors (HCs) using aqueous electrolyte and it showed high overpotential for oxygen evolution reaction[1)]. This feature realized high operating voltage of HCs up to 1.5 V, it exceeds theoretical limitation determined by potential window of aqueous electrolyte. NiO active materials with flower like structure were composed by using chemical bath deposition methods and its specific capacity was about 80 F g^{-1}. However, the electrode material was powdered state and substrate is necessary to apply for positive electrode of HCs. Heavy substrate drastically decreased the energy density of HCs.

In this work, we prepared NiO electrode by anodizing Ni sheet in the solution containing ammonium fluoride and phosphoric acid. Anodic aluminum oxide prepared by anodization of aluminum sheet in acidic solution is well known its self-assembled structure. Recent study suggests electrodes prepared by anodization of valve metals were suitable for electrochemical capacitors because oxide layers are strongly connected with current collectors. However, Ni is not valve metal and it is seems to be impossible to grow NiO layer by anodizing Ni sheets[2)]. We found the NiO layer grew on heat treated Ni substrate with anodization. We measured the electrochemical properties of the NiO layer and fabricated hybrid capacitor (HC) with the NiO layer positive electrode and activated carbon negative electrode.

Experimental

Ni sheets with the thickness of 10 μm were annealed in air at 900 ºC for 1 hour. Annealed Ni sheets were anodized at 6 V vs. Ag/AgCl in the solution containing 0.5 M ammonium fluoride in 85 wt.% phosphoric acid aqueous solution.

HC was constructed with NiO positive electrode and activated carbon negative electrode. The electrolyte solution was 10 M KOH solution. A sulfonated polypropylene separator was impregnated into 10 M KOH solutions in vacuum for 3 min and it was placed between the positive and negative electrodes. AC fiber cloth (Gun Ei Chemical Industry Co., LTD, Specific surface area: 1800 m^2 g^{-1}) was used as the negative electrode. The AC fiber cloth was dried in vacuum at 120 ºC for 10 h. After that, it was soaked into 10 M KOH solution and evacuated to remove air for 1 h. The resultant AC fiber cloth was stuck on Ni sheet substrate with carbon paste and dried at 60 °C for 1 h.

Results and discussions

Fig. 1 shows SEM images of (a) the surface and (b) cross section of NiO electrode grown on Ni sheets. The cyclic voltammetry (CV) of anodized Ni sheet in the potential range between -0.3 and 0.7 V was repeated 20 cycles before used as positive electrode, because the surface of anodized Ni sheet was consisted of fluorinated Ni and it converted to NiO after CV treatment. NiO layer with cracked structure was observed and the thickness of NiO layer was 2 ~ 3 μm. At the center of the cross section, Ni metal layer with the thickness about 4 ~ 6 μm exists. This Ni metal layer function as extremely lightweight current collector.

Figure 2 shows the CV of NiO electrode with the potential ranges between 0.3 and 0.5 V. As shown in Fig. 2, CVs showed a pseudocapacitive behavior and a couple of redox peaks were observed at 0.45 V which can be ascribed to the following reaction;

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (1)$$

Figure 3 shows the discharge capacity of HC with several current densities. The capacity of the HC was about 70 F g^{-1} at 200 mA g^{-1}. In this case, specific capacity was calculated with the weight of NiO active materials and Ni metal substrate. These features suggest our NiO electrode has suitable performance for a positive electrode for HCs.

Reference

1) H. Inoue, Y. Namba, E. Higuchi, *J. Power Sources*, 195, 6239 (2010).
2)J-H. Kim, K. Zhu, Y. Yan,C. L. Perkins, A. J. Frank, *Nano Lett*, 10, 4099 (2010)

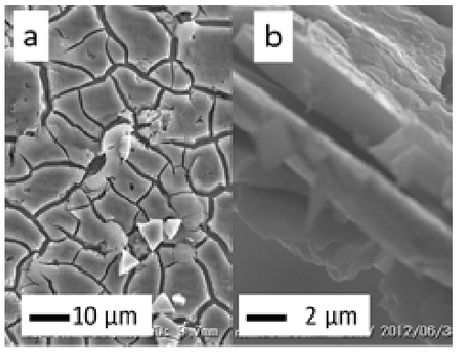

Figure 1 SEM images of NiO electrode. (a) Surface and (b) cross section

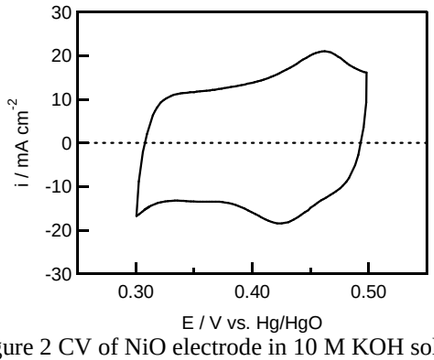

Figure 2 CV of NiO electrode in 10 M KOH solution

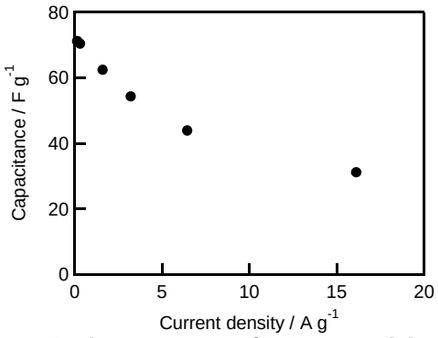

Figure 3 Discharge capacity of HC at several discharge current density.