

**Supporting Information for**

# Three-dimensional Nano-electrode by Metal-Nanowire-Nonwoven Clothes

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### **Fabrication of NiO-covered nickel-nanowire-nonwoven cloths**

The nickel-nanowire-nonwoven cloth (NNNC) was synthesized by electroless deposition. The reaction solution was prepared from nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) as a source of nickel ions, hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) as a reducing agent, trisodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) as a complexing agent, chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) as a nucleating agent, and sodium hydroxide ( $\text{NaOH}$ ) for adjusting pH of the reaction solution. These reagents were all reagent-grade (Nacalai Tesque, Inc.) and used without further purification.

First, 50  $\text{cm}^3$  of deionized water containing 0.100 M  $\text{NiCl}_2$ , 37.5 mM  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , 0.20 mM  $\text{H}_2\text{PtCl}_6$  was prepared. Then, the same amount of ion-exchanged water (50  $\text{cm}^3$ ) containing 1.00 M  $\text{N}_2\text{H}_4$  was also prepared. The pH of the both solutions was adjusted to 12.5 at 298 K using an aqueous  $\text{NaOH}$  solution. The pH of the solutions was measured using a pH meter (Horiba, Ltd., D-54). The temperature of the solutions was maintained at 353 K while the solutions were bubbled by nitrogen gas to remove dissolved oxygen. The metallic salt solution and the  $\text{N}_2\text{H}_4$  solution were mixed and maintained at 353 K in a water bath surrounded by two parallel neodymium magnets. The magnetic field strength between the magnets was set to 200 mT, as measured by a Tesla meter (KANETEC Co., Ltd., TM-601). The NNNC floated to the surface of the

reaction solution as a membrane at  $\approx 15$  minutes after mixing the solutions containing Ni(II) and hydrazine. The NNNC was washed several times with deionized water and ethanol. After drying in a desiccator, the NNNCs were annealed at 523, 543, and 573 K in air for 16 hours to obtain a NiO active material on the nanowire surfaces. The heat treatment temperature definitely affects the oxidation ratio of nickel as well as the mechanical strength of nanowires. Thus, the effect of the annealing temperature on the electrochemical performances was investigated to optimize the oxidation ratio of the nickel nanowires.

Figure 3a shows the XRD patterns of the nickel nanowires measured before and after annealing at 523-573 K for 16 h. The face-centered cubic (fcc) peaks of nickel (PDF#04-0850) are only observed before annealing. In the XRD patterns of the nanowires after anneal, both fcc Ni and the rock salt type NiO peaks (PDF#04-0835) were observed. The relative intensity of NiO peaks to Ni peaks increased with the annealing temperature. Figure 3b shows the SEM images and size distributions of the nickel nanowires. The mean diameter of the nanowires increases with annealing temperature because of the growth of the NiO layer. The mean diameter of the nanowires annealed at 573 K was 215 nm, which is 1.8 times thicker than that of pristine nanowires. Figure 3c shows the atomic ratio of oxygen to nickel (the

oxidation ratio) in NNNCs evaluated by the EDX analysis and mass measurements. The oxidation ratio of the nickel nanowires increased with annealing temperature. According to the mass measurement, the oxidation ratios were 12, 15, and 39% for the NNNC prepared at annealing temperatures of 523, 543, and 573 K, respectively. These values are in good agreement with the EDX analysis. The transmission electron microscope (TEM) images show that a thin NiO layer of 20 nm forms on the nickel nanowires annealed at 523 K (Figure 3d), indicating that NiO-covered NNNC can be fabricated by a simple two-step process using electroless deposition and annealing.

### **Material characterization**

The morphology of the nanowires was imaged using a field-emission scanning electron microscope (FE-SEM, JEOL Ltd., JSM-6500F) and a transmission electron microscope (TEM, JEOL Ltd., JEM-2010). The mean diameter and size distribution of the nanowires were determined from analysis of 200 randomly selected wires in the SEM images. The composition of the nanowires was analyzed with energy-dispersive X-ray (EDX) spectrometry. The oxidation ratio of the nickel nanowires was evaluated by measurement of the mass of the nanowires before and after annealing according to the oxidation reaction ( $2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$ ). The crystalline structure of the products

was investigated by X-ray diffraction (XRD, Rigaku Co., Ltd., RINT-2200) using Cr  $K\alpha$  radiation.

### **Electrochemical tests of NiO-covered NNNCs**

The half cells were assembled in an argon-filled glove box. The NiO-covered NNNC with an area of 16 mm in diameter was used as the working (positive) electrode. The NNNC electrode was used without any additional current collector or binder components. Li foil and polypropylene film (Celgard 2500) were used as a counter (negative) electrode and a separator, respectively. A solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a 1:2 volume ratio containing 1 M  $\text{LiPF}_6$  was used as an electrolyte. The charge-discharge profiles were measured at room temperature using a Versatile Multichannel Potentiostat (VMP3, Biologic). For the morphological observation, the electrodes were washed several times with a mixed solution of EC and DMC, and then rinsed using DMC after the charge-discharge experiments. The washed electrodes were transferred to the sample chamber of the SEM using a transfer vessel to avoid air exposure. The cyclic voltammogram was also measured by the potentiostat/galvanostat (SP300, Biologic) using a NNNC annealed at 523 K as a working electrode and Li foils as counter and reference electrodes.