Electrochemical Performance of Nanosheet-like Structured Nickel-Cobalt Oxide Thin Films

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ABSTRACT
Nickel-cobalt (Ni-Co) oxide thin films were prepared using the wet-chemical method with various growth times and their morphological and electrochemical properties were investigated. The thin films composed of the interconnected nanosheet-like structures were uniformly distributed on the surface. Electrochemical durability of the Ni-Co oxide was enhanced by increasing growth times.

1 Introduction
Hierarchical nanostructured metal oxides have been widely investigated for their morphological and electrochemical properties as electrode materials in electrochemical devices for energy storage [1,2]. In our previous study, we prepared nanosheet-like structured cobalt hydroxide (Co(OH)2) films prepared using the wet-chemical method and investigated the effects of the annealing treatment on the crystal phase and morphological property [3]. On the contrary, it was reported that the film thickness of iridium oxide (IrOx) prepared using the spray method affected the electrochemical properties [4]. Charge density and reversibility were improved as the film thickness was increased from 1200 to 3900 nm [4]. Meanwhile, the charge density of the tungsten oxide (WO3) prepared using the sol-gel was increased by increasing the certain film thickness; subsequently, it was slightly decreased owing to the grain boundaries and reaction surfaces [5].

In this study, we investigated the electrochemical performance of nanosheet-like structured nickel-cobalt (Ni-Co) oxide samples grown on fluorine-doped thin oxide (FTO)-coated glass using the simple wet-chemical method with various thin film thickness.

2 Experiment
Nickel acetate tetrahydrate (Ni(CH3COO)2·4H2O, 8 mM, Aldrich 244.66-100G), cobalt nitrate hexahydrate (Co(NO3)2·6H2O, 2 mM, Fujifilm 034-12831), and hexamethylenetetramine (HMT, C6H12N4, 5 mM, Sigma-Aldrich 398160-250G) were used without further purification [6]. An aqueous solution was stirred at room temperature for 1 h.

The FTO/glass substrate was immersed in an aqueous solution, and it was stored in an oven at 90 °C for 1—3 h. the obtained nanostructure sample was dried at 90 °C for 24 h, then annealed at 300 °C for 1 h in ambient air.

The morphological property and crystal phase of the nanostructured thin film samples were characterized using the field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD), respectively. Electrochemical properties were investigated via cyclic voltammetry (CV) in 1 M KOH electrolyte. Thin film sample, Ag/AgCl, and Pt were used as the working, reference, and counter electrodes, respectively.

3 Results & Discussion
Figure 1 (a,b) shows the FESEM images of the nanostructured samples prepared on the FTO/glass substrates. Growth time was 1 h. The nanosheet-like structures were uniformly distributed on the surface (Fig.1(a)). The film thickness was ~0.4 μm, estimated from the cross-sectional image (Fig.1(b)). As the growth time increased to 3 h (Fig.1(c,d)), the morphologies of
the nanosheet-like structures were well preserved. Distribution of the nanosheet-like structured of the sample grown for 3 h was more compact compared with that of the sample grown for 1 h (Fig.1(c)). The film thickness was increased to ~1.2 μm (Fig.1(d)). By further increasing the growth time to 6 h, the thickness of the thin film increased slightly to ~1.3 μm [6].

Figure 2 shows the XRD patterns of the nanostructured thin film samples on the FTO/glass substrate with various growth times. The diffraction peaks were observed at a 2θ position of ~26.5 °, ~33.8 °, ~38.0 °, and ~51.7 °, corresponding to the (110), (101), (200), and (211) planes of the FTO (JCPDS card No. 41-1445), respectively. This indicated that the nanosheet-like structured thin film samples are amorphous. The color of thin film samples grown for 1 and 3 h was light gray and pale yellow, respectively.

In our previous study [6], after being dried at 90 °C, the nanosheet-like structured sample was found to be composed of crystalline hydroxide. After annealing treatment at 300 °C, the phase transition from hydroxide to oxide occurred, and the nanosheet-like morphological property was well maintained.

Figure 3 shows the CV curves of Ni-Co oxide thin films prepared on FTO/glass substrates with growth time of 1 h (a) and 3 h (b). The scan rate was 50 mV/s with potential ranged between -0.15 and +0.55 V, and the area of the thin film was 1 x 1 cm. It was observed that the CV curves of both samples had a pair of redox peaks [6,7]. The CV curve area represented the charge storage capacity [5,8]. The calculated anodic (cathodic) charge density of the Ni-Co oxide grown for 1 h were 1.84 (−1.83), 3.55 (−3.52), 5.03 (−4.93), 4.90 (−4.78), and 4.77 (−4.65) mC/cm² at 100th, 300th, 600th, 800th, and 1000th cycles, respectively. By increasing the growth time to 3 h, both the anodic and cathodic charge densities increased. Maximum values were 18.18 (anodic) and −18.06 (cathodic) mC/cm² at the 800th cycle. Further increasing the CV cycle to the 1000th, the anodic and cathodic charge densities slightly decreased to 17.75 and −17.61 mC/cm², respectively. The cycle durability of the Ni-Co oxide grown for 3 h was improved compared with that of the sample grown for 1 h. On further increasing the growth time to 6 h, anodic and cathodic charge densities of 24.47 and −23.70 mC/cm², respectively, were obtained at the 1000th cycle in the potential raged between −0.20 and +0.55 V [6]. The ratio of the anodic and cathodic charge density of the Ni-Co oxide samples was closed to 1, showing high reversibility. In addition, both the Ni-Co oxide thin film samples grown for 1 and 3 h exhibited reversible color change during CV cycle.

**Fig. 2.** XRD patterns of bare FTO/glass substrate and nanosheet-like structured samples on FTO/glass substrates grown for 1 and 3 h.

**Fig. 3.** The 100th, 300th, 600th, 800th, and 1000th CV curves of the Ni-Co oxide thin films grown for 1 h (a) and (b).

4 Conclusions

The nanosheet-structured Ni-Co oxide samples were prepared on the FTO/glass substrate using the simple solution condition. By increasing the
growth time from 1 to 3 h, the thickness of thin film increased from ~0.4 to ~1.2 μm, and the nanosheet-like structures of the samples were well maintained. At CV 1000th cycle, the anodic and cathodic current densities of the Ni-Co oxide grown for 3 h were 17.75 and −17.61 mC/cm², respectively. The CV cycle durability of the Ni-Co oxide sample was improved by increasing the growth times.

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