



Short communication

Co/Al layered double hydroxides nanostructures: A binderless electrode for electrochemical capacitor

Pui Yee Loh^a, Kian Keat Lee^a, Yuting Ng^a, Chornng Haur Sow^b, Wee Shong Chin^{a,*}^a Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, 117543 Singapore, Singapore^b Department of Physics, Faculty of Science, National University of Singapore, 2 Science Drive 3, 117542 Singapore, Singapore

ARTICLE INFO

Article history:

Received 19 December 2013

Received in revised form 12 February 2014

Accepted 2 March 2014

Available online 12 March 2014

Keywords:

Cobalt

Aluminum

Layered Double Hydroxides

Electrodeposition

Pseudocapacitors

ABSTRACT

We present here a study of Co/Al layered double hydroxides (LDH) nanoflakes supported on Co nanowires as a binderless electrode for electrochemical capacitor. This nanostructured array was prepared easily via electrodeposition of Co in anodic alumina (AAO) template followed by alkaline treatment. This is the first report AAO template is used as a source of Al³⁺ to form the LDH directly. Capacitance was found to increase with the amount of Co/Al-LDH, as indicated by the Al content from EDX analysis. This content is controllable by varying the duration of alkaline treatment. High capacitance of 0.510 F/cm² was achieved for sample containing 12% Al measured at current density 2.5 mA/cm² in 1 M KOH. The electrodes also exhibited good stability, maintaining more than 90% of their original capacitance after 3000 continuous charge–discharge cycles.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical capacitors (ECs) have attracted much attention as an alternative electrical energy storage system due to their fast charging time, high power delivery or uptake in shorter times and long cycle life [1,2]. Compared to electric double-layer capacitors (EDLCs), pseudocapacitors exhibit larger capacitance, energy density and lower working voltage [3–5]. However, ruthenium oxide, which is one promising material for pseudocapacitors, is too costly for commercial use [6]. Recent development has found interests in using layered double hydroxides (LDH) as a cheaper alternative but with higher capacitive performance [7]. The structure of LDH consists of alternating layers of positively charged metal hydroxide and negatively charged counter-anions and water molecules. The positive charge of the hydroxide layer is due to partial isomorphous substitution of divalent metal cations by trivalent ones [8]. Co/Al-LDH, with Co²⁺ as the divalent ion and Al³⁺ as the trivalent ion, is among the most commonly studied LDH [9–15].

The high surface area of nanostructured materials offers more active sites, better utilization of materials and rapid transfer of electron for charge transport, all of which can improve the performance of ECs [10, 16–18]. Nanostructures comprising a combination of morphologies were recently shown to enhance electrode performance by further improving the surface area and efficiency of charge transport [19,20]. In this communication, we present a simple synthesis of Co/Al-LDH

nanoflakes (NFs) supported on Co nanowires (NWs) as a binderless electrode for ECs. The resulting electrodes were found to have large capacitance and good electrochemical stability.

2. Experimental

Electrodeposition was carried out using Autolab PGSTAT30 potentiostat/galvanostat in a three-electrode configuration (Pt rod as counter electrode (CE), Ag/AgCl (3 M KCl) as a reference electrode (RE) and a thin layer of gold sputtered on one side of the anodic aluminum oxide (AAO) template as working electrode (WE)). The AAO/Au was secured on a copper plate using copper conductive tape and placed into a Teflon cell with a hole of 1 cm diameter. This hole, secured by Kalrez® rubber O-ring, defined the area of AAO in contact to the plating solution.

Co NWs were electrodeposited into the AAO template at constant current of -1.5 mA from aqueous solution of 266 g/L CoSO₄·7H₂O and 40 g/L H₃BO₃. The sample was then immersed in 2.5 M NaOH for varying durations. In most procedures, such alkaline treatment removes the AAO template after electrodeposition. We have found in this study, and also with reference to our earlier work [21,22], that such alkaline treatment will produce Co hydroxides and Co/Al-LDH NFs at the same time, providing a one-step synthesis of a binderless LDH electrode.

Morphology and Al content of the resulting nanostructures were characterized using JEOL JSM 6701-F Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX) detector. X-ray diffraction (XRD) patterns were recorded on Philips diffractometer using Cu K α radiation ($\lambda = 1.54187$ Å).

* Corresponding author.

E-mail address: chmcws@nus.edu.sg (W.S. Chin).

For electrochemical analysis, an electrochemical half cell was assembled with Pt rod as CE, Ag/AgCl (3 M KCl) as RE and the above prepared sample as WE. Cyclic voltammetry (CV) and galvanostatic charge-discharge (C-D) measurements were carried out in 1 M KOH at ambient condition using Autolab PGSTAT30 potentiostat/galvanostat. From the C-D curves, area-specific capacitance, C_a (F/cm^2) = $(I_d \times \Delta t) / \Delta V$ can be calculated, where I_d (A/cm^2) = discharge current density, Δt (s) = discharge time and ΔV (V) = discharge potential range.

3. Results and discussions

3.1. Characterizations

Uniform Co NWs of specific length can be grown within the AAO template in a controllable manner via constant current deposition. In this study, Co NWs of about $5 \mu\text{m}$ electrodeposited at 90 min were used throughout. After the alkaline treatment, NFs were observed on both the top and sides of the NWs (Fig. 1A–D). These NFs could arise from the corrosion of Co NWs in the concentrated alkaline solution, leading to the precipitation of less soluble $\text{Co}(\text{OH})_2$ [23]. Since Al^{3+} was formed in the solution during the simultaneous dissolution of

AAO template, some Al^{3+} ions could isomorphously substitute Co^{2+} during hydroxide formation to give Co/Al-LDH. Generally, more NFs were formed with longer alkaline treatment time, especially on top of the NWs array. Moreover, the NF crystals also appeared larger and the hexagonal shape became more defined for prolonged alkaline treatment (insets of Fig. 1A–D). The growth of crystals in the gaps between the NWs may be limited by diffusion to replenish the depleted OH^- ions.

The Al content in atomic percentage ratio, i.e. $x = \text{Al} / (\text{Al} + \text{Co})$, was estimated from EDX analysis and given in Fig. 1A–D. It was found to increase with the duration of alkaline treatment but the increase seems to slow down after 24 h. This is expected since the supply of Al^{3+} was limited by AAO template. The formation of Co/Al-LDH was confirmed by XRD diffraction patterns (Fig. 1E). Characteristic peaks of Au, Co and Cu are due to the Au substrate, Co NWs and Cu tape, respectively. The remaining XRD patterns match well with characteristic peaks of $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ hydroxalcalitic phase (JCPDS 00-051-0045). Generally, these peaks became more intense for samples treated for longer duration. The increasing XRD peak intensities and Al contents suggest that LDH species is increasingly dominant on the surface along the series of samples prepared. For

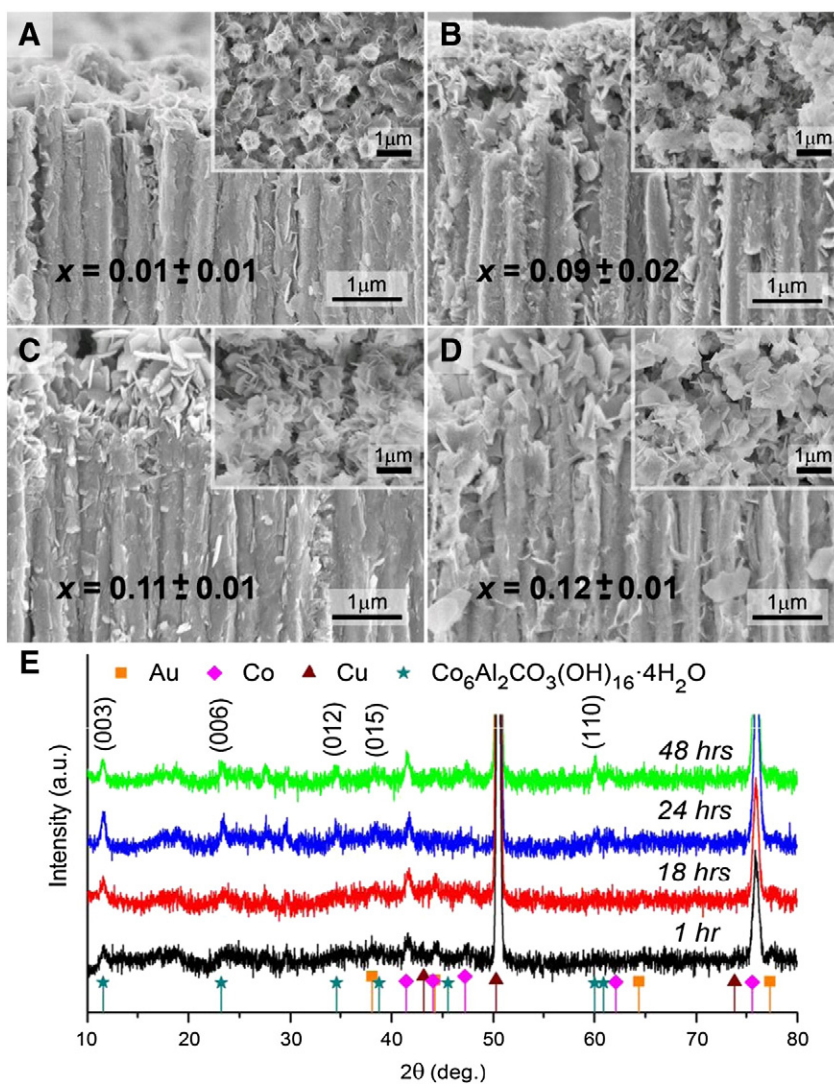


Fig. 1. Side view SEM images of samples after alkaline treatment for (A) 1, (B) 18, (C) 24 and (D) 48 h with the Al content, x , as labeled. Insets in (A)–(D): top views for the respective samples. (E) XRD patterns of Co/Al-LDH samples. Reference peaks: Au (JCPDS 01-071-4614), Co (JCPDS 01-071-4652), Cu (JCPDS 01-071-4611) and $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS 00-051-0045).

Download English Version:

<https://daneshyari.com/en/article/179017>

Download Persian Version:

<https://daneshyari.com/article/179017>

[Daneshyari.com](https://daneshyari.com)