



# Directly growing hierarchical nickel-copper hydroxide nanowires on carbon fibre cloth for efficient electrooxidation of ammonia



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## ARTICLE INFO

### Article history:

Received 17 February 2017

Received in revised form 28 June 2017

Accepted 3 July 2017

Available online 4 July 2017

### Keywords:

Hierarchical  
Layered hydroxide  
Electrocatalyst  
Nano-wire  
Ammonia oxidation

## ABSTRACT

Ammonia is an attractive carbon-free chemical for electrochemical energy conversion and storage. However, the sluggish kinetic rates of the ammonia electrooxidation reaction, and high cost and poisoning of Pt-based catalysts still remain challenges. This also limits the development of direct ammonia fuel cells. In this work, we directly grew hierarchical mixed NiCu layered hydroxides (LHs) nanowires on carbon fibre cloth electrodes by a facile one-step hydrothermal synthesis method for efficient electro-oxidation of ammonia. This catalyst achieves a current density of  $35 \text{ mA cm}^{-2}$  at 0.55 V vs. Ag/AgCl, which is much higher than that of bare  $\text{Ni}(\text{OH})_2$  catalyst ( $5 \text{ mA cm}^{-2}$ ). This is due to abundant active sites and a synergistic effect between Ni and Cu, possibly due to the formation of  $\text{Ni}_{1-x}\text{Cu}_x\text{OOH}$  on the surface of the catalysts through the electrochemical activation of the mixture of  $\text{Cu}(\text{OH})_2$  and  $\alpha\text{-Ni}(\text{OH})_2$ . In the investigated first row transition elements, it is found that Cu is the sole first-row transition metal to effectively improve activity of  $\text{Ni}(\text{OH})_2$  for ammonia electrooxidation. This mixed NiCu LHs nano-wire catalyst outperforms commercial Pt/C catalyst in the aspects of ammonia oxidation current and stability, demonstrating it to be a promising low-cost and stable catalyst for efficient ammonia electrooxidation in alkaline condition, which is a potential electrode for ammonia fuel cells for power generation or electrolysis of ammonia for ammonia-containing wastewater treatment.

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## 1. Introduction

Ammonia is regarded as a carbon-free hydrogen-storage material with a hydrogen weight percent of 17.6 wt% [1–3]. Direct electrooxidation of ammonia at room temperature has wide applications in energy conversion and storage such as direct ammonia fuel cells and hydrogen fuel production [4–7]. In theory, the energy required in ammonia electrolysis (0.06 V) is 95% less than the required energy cost in water electrolysis (1.23 V) for hydrogen production [8]. Besides, it is also a promising technology to remove nitrogen for wastewater remediation [8]. However, the main challenge of ammonia electrooxidation is sluggish kinetic rates. Until now, Pt and Pt-based catalysts for ammonia electrooxidation have been extensively investigated due to their low

overpotential [9–14]. However, the ammonia poisoning and high price of Pt still remain a barrier for its large-scale application [15].

Due to the challenges listed above, many research works aim to develop Pt-free catalysts with high activity and stability for use in the ammonia electrode [15]. Nickel is a much more earth-abundant and therefore affordable to use as an electrode material for electrochemical devices. However, it has been found that it is inactive toward ammonia electrooxidation [16,17]. Nevertheless, Kapałka et al. discovered that ammonia could be catalytically oxidized on  $\text{Ni}(\text{OH})_2$ , which was generated through the electrooxidation of the Ni electrode in alkaline conditions [18]. They explained that the ammonia electrooxidation on  $\text{Ni}(\text{OH})_2$  was attributed to the electrocatalytic reaction on  $\text{NiOOH}$ , which could be formed via a reversible electrochemical reaction between  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  [19,20]. Although  $\text{Ni}(\text{OH})_2$  shows good catalytic property as a Pt-free electrode, it still has disadvantages such as electrode stability and the concomitant release of Ni to the electrolyte [18].

Transition metal based electrocatalysts and metal-organic electrocatalysts have been reported to be promising alternatives to

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noble metals [21,22]. Recently, the first-row transition metal based layered hydroxides (LHs) with brucite like layers have attracted much attention in electrochemical energy applications [23–27]. Among them, nickel based LHs have been widely investigated in water electrolysis in alkaline conditions. The catalytic activity of Ni-based LHs is largely dependent on the doping element. So far, NiFe and NiV LHs have proven to show the best catalytic performance in water electrolysis [28–30]. Other dopants, including Mn and Cr, can also improve catalytic activity but to a lesser extent than Fe and V [24]. Contrary to the promotion observed from other dopants, the incorporation of Co, Cu and Zn has been shown to reduce the catalytic activity to electrolysis of water [24].

Although it has been reported that pure Ni(OH)<sub>2</sub> has good catalytic activity to electrochemical oxidation of ammonia [18], to the best of our knowledge, reports on Ni-based LHs for ammonia electrooxidation are scarce. Introduction of another element in layered hydroxides will significantly change the catalytic properties as described above. In a recent study, we found that NiCu bimetal exhibit excellent catalytic activity toward electrochemical oxidation of ammonia [31]. Actually, we found that after electrochemical activation NiCu would be transformed from bimetal to hydroxides, which were the final effective catalysts. In this study, instead of preparing bimetal, we directly prepare the hydroxides, i.e., the real active catalysts through a facile hydrothermal synthesis process. It was found that the nickel copper hydroxides still exhibit the best catalytic activity, and the oxidation current density was improved when compared to nickel copper bimetal, which further confirm nickel copper hydroxide is an excellent catalyst for electrochemical oxidation of ammonia. Here we choose Cu as the dopant in order to prepare NiCu LHs. Cu was chosen as it is theoretically predicted to be one of the most active metals for ammonia electrooxidation [32]. Although previous work shows bare Cu is almost inactive toward ammonia electrooxidation as Cu binds N atoms too weakly leading to a very high overpotential [33], NiCu LHs are expected to perform well due to a synergistic effect between Cu and Ni, since Ni binds N atoms strongly [32]. In this work, we synthesised hierarchical NiCu LHs with nano-wires structure on carbon fibre cloth via a facile hydrothermal reaction followed by electrochemical activation but the final products are a mixture of Cu(OH)<sub>2</sub> and Ni(OH)<sub>2</sub>. The mixed layered Cu(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> catalysts could be converted into Ni<sub>1-x</sub>Cu<sub>x</sub>OOH by electrochemical activation, which shows much higher activity than pure Ni(OH)<sub>2</sub> catalyst, and even outperform the commercial Pt/C catalyst. For comparison, other first-row transition metals including Cr, Mn, Fe, Co, Zn are also used as dopants to prepare Ni-based LHs respectively. It was found that, among these elements, Cu is the unique element which can significantly improve catalytic activity towards electrooxidation of ammonia. The synthesised nickel-copper hydroxide also exhibit hierarchical microstructure which can maximise the surface area to further increase the catalytic activity [34,35].

## 2. Experimental section

### 2.1. Materials

Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Alfa Aesar), and copper(II) nitrate hemi(pentahydrate) (Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, 99.0%, Alfa Aesar) were utilized without any further purification. Plain carbon fibre cloth (0.35 mm thickness, E-TEK) was used as substrate for the catalysts. Carbon fibre cloth electrode (1 × 3 cm<sup>2</sup>) was first cleaned using HCl and ethanol, before being rinsed with deionized water as a pre-treatment before the hydrothermal reaction in an autoclave. Nafion<sup>®</sup> solution (5 wt%) were purchased from Sigma-Aldrich. Other chemicals including Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O,

NH<sub>4</sub>Cl, urea, isopropanol and NaOH were all analytical reagents and bought from Alfa Aesar. Pt/C (20 wt.%) was also bought from Alfa Aesar.

### 2.2. Preparation of Ni-based LHs

Hierarchical nickel-copper LHs were directly formed on a carbon fibre cloth (CFC) electrode via a one-step hydrothermal method. Briefly, 20 mL of metal precursor solution consisting of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions was prepared by mixing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O in deionized water. To study the effect of Cu proportion, different mole ratios of Ni<sup>2+</sup>/Cu<sup>2+</sup> metal precursor solution (1:0, 9:1, 4:1, 7:3, 3:2 and 1:1, with correspondingly obtained samples named bare Ni(OH)<sub>2</sub>, Ni<sub>0.9</sub>Cu<sub>0.1</sub> LHs, Ni<sub>0.8</sub>Cu<sub>0.2</sub> LHs, Ni<sub>0.7</sub>Cu<sub>0.3</sub> LHs, Ni<sub>0.6</sub>Cu<sub>0.4</sub> LHs and Ni<sub>0.5</sub>Cu<sub>0.5</sub> LHs, respectively) were employed, while the total amount of metal ions (Ni<sup>2+</sup> and Cu<sup>2+</sup>) was kept at 1 mmol 75 mg of urea was then added to the aqueous mixed metal nitrate solution. After stirring for 10 min, the mixture solution was transferred to a Teflon-lined stainless steel autoclave. The carbon fibre cloth electrode was then soaked in the solution, followed by heating at 120 °C for 14 h in an oven. The as-synthesised electrodes were washed using deionized water and ethanol four times, after which they were then dried at 60 °C in a vacuum oven overnight. The catalyst loading on the electrode was calculated by the weight difference of carbon fibre cloth electrode after and before hydrothermal synthesis.

In this work, other transition metals were also used to prepare NiM LHs (M = Cr, Mn, Fe, Co, Zn, respectively). In order to synthesise the NiM LHs a similar method to that of NiCu LHs was used with copper nitrate replaced by other metal nitrates. All the mole ratios of Ni/M in the metal precursor solutions were fixed to 1:1.

For comparison, carbon supported Pt (Pt/C) particles were ultrasonically dispersed in a mixture of Nafion<sup>®</sup> solution, isopropanol and deionized water in order to get the catalysts ink. It was then brushed onto a carbon fibre cloth electrode to prepare Pt/C electrodes for comparison. The Pt loading on the carbon fibre electrode was 0.4 mg cm<sup>-2</sup> [36].

### 2.3. Characterization

X-ray diffraction (XRD) analysis (Panalytical X-Pert Pro MPD with Cu K<sub>α1</sub> radiation) was used to examine the phases of the samples. X-ray photoelectron spectroscopy (XPS) data were collected using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, UK), with samples being illuminated using an Al K<sub>α</sub> x-ray source and photoelectrons collected using the detector at a resolution of approximately 0.4 eV. A charge neutraliser was used to negate the effects of differential charging of the surface during the experiment, with binding energies subsequently referenced to the C 1s energy level at 284.85 eV. The microstructure and morphology were examined using a scanning electron microscope (SEM, Zeiss SUPRA 55-VP) equipped with an energy-dispersive X-ray (EDX) spectrometer that allows elemental composition analysis. Transmission electron microscopy (TEM) was conducted by using JEOL 2100.

Electrochemical characterization was performed in a three-electrode system at room temperature, where the catalyst coated carbon fibre electrode was the working electrode, Pt foil was used as the counter electrode and Ag/AgCl as the reference electrode. All electrodes were connected to a Solartron 1287A electrochemical station in order to conduct the electrochemical measurements. Before testing, all samples were electrochemically activated by potential cycling between -0.2 V and 1.0 V vs. Ag/AgCl (200 scans), at 50 mV s<sup>-1</sup> of scan rate in 0.5 M NaOH at room temperature. The cyclic voltammetry (CV) measurements, from 0 V to 0.8 V with a scan rate of 25 mV s<sup>-1</sup>, were recorded after at least 3 cycles to

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