



Electrochemical actuation of nickel hydroxide/oxyhydroxide at sub-volt voltages

Kin-Wa Kwan, Nga-Yu Hau, Shien-Ping Feng, Alfonso Hing-Wan Ngan*

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China

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ABSTRACT

The development of materials capable of actuating at low triggering voltages is crucial for applications such as compact prime movers for soft, micro robots. In this paper, the electrochemical actuation of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ in alkaline environment at low voltages is demonstrated and studied for the first time. Specifically, sub-micron layers of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ deposited on Ni films a few microns thick by anodic electrodeposition were found to undergo reversible contraction by $\sim 0.1\%$ in an alkaline solution under a low voltage of only $\sim 0.4\text{V}$, causing a 5-mm long bi-layer actuator to bend by $\sim 3.5\text{mm}$ at its end, giving a large device strain of $\sim 70\%$. The actuation mechanism is found to be due to a redox reaction in the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple. By masked electrodeposition, successful fabrication of actuators of various shapes and actuation performance was also demonstrated. The required electrolyte can be packaged with the actuating material to achieve a stand-alone actuating device.

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1. Introduction

The last two decades have seen a surge in interest on developing small, compact and self-contained actuating materials for applications as artificial muscles, to replace bulky pneumatic or hydraulic actuators, motors or engines, for robotics [1]. Conventional piezoelectric ceramics actuate with large rate response of $>10\%/s$ and good strains of $\sim 0.1\%$ which is already close to the elastic limit of the material, but they do so only under high triggering voltages typically in the kV range [2–4]. Dielectric elastomers also show similar rate response and even much larger actuating strains, but again, they typically require kV voltages to actuate [5–9]. The kilo-volt requirements of these materials make them unsuitable for compact designs, as in micro-robots. Of other known types of actuating materials, a few can actuate at low voltages in the 1–10 V range. Conducting polymers can actuate from less than a volt to a few volts giving good strains of a few%, but their rate response is slow due to the reliance on ion diffusion within the polymer to cause actuation [10–13]. Carbon nanotubes can also actuate at a few volts, with both good strain and rate responses [14–17]. Nanoporous noble metals such as Au and Pt are known to actuate in electrolytic environments under low voltages by changes in surface stress associated with the electrical double layer (EDL) at the electrolyte-metal interface [18–22]. On the other hand, nanoporous

Ni, as a non-noble metal much cheaper than noble counterparts, has also been found to exhibit electrochemical actuation [23–26]. Cyclic voltammetry and electrical impedance spectroscopy indicated that a redox couple on the Ni surfaces is responsible for the electrochemical actuation [24–26], and $\text{Ni}(\text{OH})_2/\text{NiOOH}$ was suggested as such a possible redox couple [24–26], although no concrete proof has been obtained so far.

The redox couple $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ is a well-known material system for use as electrodes in nickel-metal hydride rechargeable batteries, in addition to other usages including catalysts and sensors [27]. While the redox reaction in Ni hydride rechargeable batteries during charging and discharging can cause mechanical swelling and shrinkage in the electrode which will limit the life of the battery [28–31], in the present work, we explore a promising use of such electrochemomechanical effects as electrochemical actuators. Specifically, the unit cell volume of $\text{Ni}(\text{OH})_2$ can decrease by more than 10% when oxidized into NiOOH [32], and reversible redox zipping between the two phases $\text{Ni}(\text{OH})_2$ and NiOOH is known to happen within low voltage ranges of less than one volt [33,34]. Such remarkable properties should make $\text{Ni}(\text{OH})_2/\text{NiOOH}$ a promising material system for electrochemical actuation under low triggering voltages. In this work, we successfully demonstrate that $\text{Ni}(\text{OH})_2/\text{NiOOH}$ directly fabricated by anodic electrodeposition on Ni films can undergo highly reversible and stable electrochemical actuation under low voltages of only $\sim 0.4\text{V}$ in an alkaline medium, with the intrinsic actuation strain higher than 0.1%. Through proper device engineering, we also demonstrate that high device strains approaching unity can be produced from the intrinsic actuation

* Corresponding author.

E-mail address: hwngan@hku.hk (A.H.-W. Ngan).

strain of such a material system. Furthermore, by applying masked electrodeposition in the fabrication, Ni(OH)₂/NiOOH actuators of various shapes can be built. These show that Ni(OH)₂/NiOOH is a promising and versatile material system for developing artificial muscles for soft or micro robots.

2. Experimental

2.1. Fabrication of the actuators

Ni(OH)₂/NiOOH was deposited on thin films of Ni metal the fabrication of which is first described here. The Ni films were plated on fluorine doped tin oxide (FTO) glass by a Ni Plating Kit (Caswell) using a CHI 660E (CH Instruments) electrochemical workstation. To make actuators of a cantilever shape, a mask of 50 μm-thick chemical-resist sticker (Max Bepop, CM-200E) with rectangular cuts of 1 mm × 15 mm was first adhered to the FTO. The plating bath was a 3-electrode electrolytic cell using a Pt mesh counter electrode. Voltages of −1.2 V vs SCE for various durations ranging from 3.75 min to 12.5 min were applied to obtain different Ni thickness t_{Ni} . After rinsing by DI water, rectangular Ni films with a smooth and shiny surface were obtained.

For the electrodeposition of Ni(OH)₂/NiOOH, lacquer was first painted on the Ni films (still supported by FTO) so that only 1 mm × 5 mm areas would be plated with Ni(OH)₂/NiOOH. The same 3-electrode plating bath and electrochemical workstation were used, with the solution changed into 0.13 M NiSO₄, 0.1 M NaOAc and 0.13 M of Na₂SO₄. The plating anodic current density used was mainly 0.4 mA/cm² for 30 min under vigorous stirring. A uniform black or dark brown layer, which was subsequently characterized to be Ni(OH)₂/NiOOH, was observed. Other current densities (from 0.04 to 1 mA/cm²) and plating durations (from 5 to 50 min) were also studied. After rinsing and detaching the lacquer and mask by tweezers, the rectangular bilayers comprising Ni(OH)₂/NiOOH on top of Ni films were carefully peeled off from the FTO. The uncoated region of Ni was attached to Cu tape (3M™) to form the cantilever-actuators as shown in the inset of Fig. 1a. For each plating parameter, 5 samples were made and each was tested for 10 cycles under cyclic voltammetry, giving 50 measurements for the end-deflection data. The data points in Fig. 3 are obtained from the mean of the end-deflection normalized with the length of the actuator, with the error bars indicating the standard deviations.

2.2. Actuation tests

The actuation tests were carried out in a 3-electrode cell (Fig. 1a). In each test, a cantilever-actuator was held vertically as shown. Voltage was applied to the actuator by an electrochemical workstation (LK2006A, Lanlike) under 1 M NaOH against SCE reference electrode. The end-deflection of the cantilever-actuators was video-recorded by a compact digital camera (DSC-H70, Sony Co.). For some actuators with smaller end deflections, an optical microscope (Olympus Co.) was used. A CCD camera (DXC-107P, Sony Co.) was connected to the microscope via a microscope attachment (WV-9005, Matsushita Comm. Industrial Co. Ltd). The captured videos were processed by a computer freeware Kinovea to obtain the numerical data for the end-deflection measurement. Fig. 1b,c show the schematic diagram and photographs of an actuator undergoing reduction and oxidization during the test.

2.3. Characterization of the actuators

The thickness of the Ni substrate was measured by a DektakXT[®] stylus profiler (Bruker). Microstructural characterization was carried out by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy

(XPS) and X-ray diffraction (XRD). A Leo 1530 FEG SEM and a Hitachi S4800 FEG SEM were used to image the surface morphologies and thickness of the Ni(OH)₂/NiOOH. TEM imaging and selected area electron diffraction (SAED) were performed by a JEOL 2010 TEM. The TEM samples were prepared by oxidizing or reducing the electrodeposited Ni(OH)₂/NiOOH in 1 M NaOH for 30 min at 0.4/0 V vs SCE. Then, the Ni(OH)₂/NiOOH layer was scratched off from the Ni substrate and adhered onto a formvar film.

XPS was performed in a Kratos Axis Ultra Spectrometer using a monochromatic Al K α source. Glazing incidence XRD was performed in a Rigaku Smartlab diffractometer with an incidence angle of 0.5° using a monochromatic Cu K α source ($\lambda = 1.5406 \text{ \AA}$). In addition to the oxidized/reduced Ni(OH)₂/NiOOH samples described above, a bare Ni sample prepared by the first electrodeposition step was also characterized for comparison purposes.

3. Results

3.1. Actuation behavior

Bilayered cantilevers comprising a thin layer of the Ni(OH)₂/NiOOH actuating material backed by a passive Ni layer were fabricated as described in Experimental section. On applying a positive potential to the cantilever actuators in 1 M NaOH solution as shown in Fig. 1a, they exhibit large bending towards the side of the Ni(OH)₂/NiOOH layer, corresponding to contractive actuation of the latter (Fig. 1b,c). The actuation is reversible during potential cycling, as shown in the example in Supplementary Movie 1. Accompanying the actuation, the color of the Ni(OH)₂/NiOOH layer also turned slightly darker upon oxidation (increasing) and paler upon reduction (decreasing potential), as shown in Supplementary Movie 2—the color change here is a good indication of an electrochemical reaction. The end-deflection per unit length of the cantilever-actuator (D/L), used here as a measure of the device strain of the cantilever-actuator, was measured under cyclic potential scanning from 0 to 0.425 V vs SCE at a rate of 25 mV/s. The results are plotted against the applied voltage for different Ni film thickness t_{Ni} in Fig. 2a. The actuation was faster for smaller t_{Ni} , with the highest D/L reaching ~0.7 for the smallest $t_{Ni} = 1.3 \text{ \mu m}$ studied. The hysteresis in the response is likely caused by time-dependent factors including kinetic, mass-transfer and ohmic resistances, as quasi-reversibility is observed from the cyclic voltammetry, where the ratio of peak currents for oxidation to reduction is smaller than 1 and the difference in the peak potentials is larger than 59 mV [35]. Also, redox reaction of Ni(OH)₂/NiOOH was shown to exhibit time-independent hysteresis, which is thought to be caused by the ion intercalation or phase separation during the reaction [36].

The cyclic voltammetry (CV) in Fig. 2b indicates clearly a redox reaction with an oxidation peak at ~0.37 V and a reduction peak at ~0.25 V, which are broadly similar to other CV reported for the redox couple Ni(OH)₂/NiOOH in the literature [34,37]. The charge transfer to the actuator from the workstation was calculated by integrating current over time, and as shown in Fig. 2c, the rise and fall of the charge transferred, which corresponds to the progression of the oxidation reaction (i.e. amount of oxidant formed) according to the Faradaic law, coincide with the rise and fall of D/L , indicating that the actuation was mainly caused by the redox reaction, as a result of the volume decrease on oxidation. Fig. 2d shows the D/L and the voltage applied over 10 typical cycles for the 1.3 μm t_{Ni} actuator. Fig. S2 in the Supplementary Information shows the last 36 cycles of a 100-cycle test under 0.2–0.36 V vs SCE voltage cycling at 25 mV/s, for a 1.3 μm t_{Ni} cantilever-actuator which had been tested for 400 cycles in prior. The D/L is very steady, indicating the high stability of the system.

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