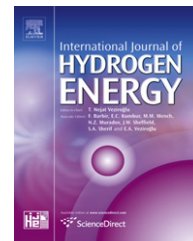


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# Enhanced electrochemical performance of nickel hydroxide electrode with monolayer hollow spheres composed of nanoflakes

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## ABSTRACT

Nickel hydroxide electrodes with hollow spheres were fabricated using a PS (polystyrene) sphere template and electrochemical deposition. The nickel hydroxide grew perpendicular to the electrode substrate during anodic deposition and around the PS spheres during cathodic deposition. After the removal of the PS template, hollow spheres or open hollow spheres were formed via cathodic deposition. The nickel hydroxide electrode with hollow spheres and nanoflakes showed greatly enhanced electrochemical performance in alkaline solution compared with the bare nickel hydroxide electrode. The opening of the hollow spheres facilitated easy electrolyte transport to the reaction sites and led to a further increase in the specific capacitance of the nickel hydroxide electrode. The specific capacitance of the electrode with the open hollow spheres reached  $800 \text{ F g}^{-1}$ , which was much higher than that of the bare electrode ( $224 \text{ F g}^{-1}$ ) and the hollow-sphere electrode ( $342 \text{ F g}^{-1}$ ) at a discharge current density of  $10 \text{ A g}^{-1}$ .

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## 1. Introduction

Nickel hydroxide nanostructures have recently received considerable attention because of their potential applications in energy storage devices such as nickel-hydrogen batteries, nickel-metal hydride batteries, nickel-cadmium batteries, and supercapacitors [1,2]. A porous structure is a factor of considerable importance in improving the electrochemical performance of nickel oxide/hydroxide electrodes because it can provide more paths for electrolytes and ions to move through the pore channels [3]. In addition, a high surface area and large pore volume are essential to achieve superior electrode performance. Nanoflake-like nickel oxide/hydroxide materials have been reported to exhibit high surface areas and suitable pore sizes for application in electrode materials [4–6]. An

electrode with macropores allows fast charging and discharging without significant capacity loss. Our previous work demonstrated that macropores, particularly open macropores, play an important role in enhancing the electrochemical performance of nickel oxide/hydroxide electrodes [7–9].

Macroporous structures such as core-shell and hollow-sphere nanostructures are widely considered to be effective for application in high surface area electrodes [10,11]. Hollow-sphere materials are typically fabricated via a colloidal template technique, which is a facile technique used to tailor the shape and size of outside materials by using different templates. With sphere templates, including those composed of polystyrene (PS) or silica spheres, the active electrode materials can be coated on the spheres to form a core-shell structure. The hollow-sphere materials can be readily

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obtained by removing the core materials by solvent or thermal decomposition. Electrochemical deposition is believed to be an effective method for the fabrication of core-shell nanostructures or three-dimensional ordered macroporous materials using colloidal templates [12,13]. Electrochemical deposition can be used to control both the growth rate and the thickness of the resulting material by controlling the charge passed, reaction potential, and concentration of reactants. The active materials can be electrodeposited inside the template voids and around the surface of the colloid particles during deposition. Cathodic electrodeposition is commonly used to prepare core-shell structures of metal oxides such as PS/nickel hydroxide [14,15], PS/zinc oxide [16–18], PS/cerium oxide [19,20], PS/tin oxide [21], PS/cobalt oxide [22], and PS/conducting polymer [23,24].

In the present work, we reveal that the morphological evolution of porous nickel hydroxide depends on the polarity of the applied potential (cathodic or anodic) during deposition using a negatively charged PS template. Nickel hydroxide was deposited in the interstitial spaces between PS spheres during anodic deposition and around the surface of the PS spheres during cathodic deposition. A possible deposition mechanism used to explain the potential-dependent variation of the deposits is discussed. The electrochemical performance of macroporous nickel oxide electrodes prepared by anodic electrodeposition has been previously investigated by our group [7,9]. In this work, the electrochemical performance of a nickel hydroxide electrode composed of hollow spheres prepared by cathodic deposition was studied. In addition, it was determined that a nickel hydroxide electrode with open spheres can be easily achieved by tuning the charge passed during cathodic deposition. We expect that the tailored structure featuring open hollow spheres may facilitate electrolyte and ion transport within the electrode and may consequently enhance the electrode performance.

## 2. Experimental

A monolayer PS-sphere template was assembled onto a stainless steel (SS) substrate by EPD (electrophoretic deposition). The EPD method provides an efficient approach for the deposition of templates with controlled thickness and homogeneous microstructure on conductive substrates [25]. Monodispersed PS spheres (with negatively charged surfaces) of approximately 200 nm in diameter were suspended in water (2.5 wt.%, Alfa Aesar). EPD of the monolayer PS template was carried out by applying a voltage difference of 60 V (Keithley, 2400 source meter) between working (positive electrode, SS, 2 × 2 cm) and counter (negative electrode, platinum, 2 × 2 cm) electrodes for 30 s. An EPD bath was prepared by suspending IPA (50 ml) in a PS suspension (16 mg, 2.5 wt.%). Prior to deposition, the SS substrate was cut into pieces 2 × 2 cm in dimension, which were then soaked in acetone and ultrasonically vibrated for 10 min to wash away any contaminants from their surfaces. De-ionized water was then used to rinse the tailored SS substrate via ultrasonic vibration for another 15 min. The distance between the working and counter electrodes was maintained at 1 cm. After EPD, the PS-coated SS electrode was dried at room temperature for 24 h in air.

Nickel hydroxide films were electrodeposited directly onto the PS-sphere-coated SS substrate and bare SS substrate at room temperature. The potentials applied for anodic and cathodic deposition were set to 0.9 V and –0.9 V versus a saturated calomel electrode, respectively. The anodic deposition bath consisted of 0.13 M sodium acetate, 0.13 M nickel sulfate, and 0.1 M sodium sulfate. The cathodic deposition bath consisted of 0.1 M nickel nitrate and 0.1 M potassium nitrate. The electrochemical deposition of nickel hydroxide was carried out in a three-compartment cell. A saturated calomel electrode was used as the reference electrode, and a platinum foil with dimension 2 × 2 cm was used as the counter electrode. All chemicals were of analytical grade and were used without further purification. The plating solution was stirred by a Teflon stir bar on a magnetic hot plate during the deposition. After deposition, the nickel hydroxide electrode was rinsed several times in de-ionized water and then immersed in a toluene solution for 10 min to remove the PS-sphere template. The resultant porous nickel hydroxide electrode was dried at 100 °C for 1 h in air. The amount of deposited nickel hydroxide was measured by a microbalance (Mettler, XS105DU) with an accuracy of 0.01 mg.

The surface morphology of the electrodeposited nickel hydroxide electrodes was examined with a field-emission electron microscope (FE-SEM, Jeol JEOL-6330) with an accelerating voltage of 3 keV. The crystal structure of the electrodeposited nickel hydroxide scraped from the SS substrate was identified by X-ray powder diffraction (XRD, Rigaku, D-MAX 2200) with a Cu K $\alpha$  target (wavelength = 1.54056 Å).

The electrochemical behavior of the nickel hydroxide electrodes was determined by cyclic voltammetry and galvanostatic charge-discharge test in a three-electrode cell with a 0.5 M KOH electrolyte. A saturated Ag/AgCl electrode was used as the reference electrode and a platinum foil with dimensions of 2 × 2 cm as the counter electrode. The potential was cycled at a scan rate of 1 mV s<sup>-1</sup> using a potentiostat (CH Instruments, CHI 608) over a range of 0–0.45 V. The electrode was charged at a current density of 1 A g<sup>-1</sup> to a cut-off potential of 0.45 V. The fully charged electrode was discharged at various current densities to a cut-off potential of 0.0 V.

## 3. Results and discussion

Fig. 1 illustrates the formation mechanism of the porous nickel hydroxide electrodes using anodic and cathodic methods. The monolayer PS-sphere template was assembled by the EPD strategy before the formation of nickel hydroxide. The anodic formation of nickel hydroxide depends on the oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup>, which further reacts with the available hydroxide ions from a slightly alkaline electrolyte to form nickel hydroxide nanoflakes on the exposed SS substrate surface [26]. The PS spheres have negatively charged surfaces on which nickel ions can be absorbed due to the electrostatic force between PS and nickel ions. However, it is difficult to directly deposit nickel hydroxide on the PS surface because PS is an electrical insulator, which cannot conduct electrons for the electrochemical reaction to occur. When the nickel ions in the bulk electrolyte arrive at the exposed SS surface due to

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