## Nickel oxide film with open macropores fabricated by surfactant-assisted anodic deposition for high capacitance supercapacitors<sup>†</sup>

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*Received 29th June 2010, Accepted 26th July 2010* DOI: 10.1039/c0cc02180f

Nickel oxide film with open macropores prepared by anodic deposition in the presence of surfactant shows a very high capacitance of 1110 F  $g^{-1}$  at a scan rate of 10 mV  $s^{-1}$ , and the capacitance value reduces to 950 F  $g^{-1}$  at a high scan rate of 200 mV  $s^{-1}$ .

Supercapacitors have attracted a great deal of attention from researchers because of their high power density and long life cycle compared to traditional batteries.<sup>1</sup> Previous reports have demonstrated that metal oxides such as ruthenium oxide,<sup>2</sup> nickel oxide,<sup>3</sup> manganese oxide,<sup>4</sup> and cobalt oxide<sup>5</sup> can meet the requirements of capacitor materials. Among these oxide materials, nickel oxide is a promising candidate for alkaline supercapacitors due to its unique physical and chemical properties in alkaline electrolyte.

Porous structure is a crucial factor in determining the capacitive behavior of the nickel oxide. The mesoporous structure has been shown to increase the capacitance of nickel oxides due to the larger effective surface area of the mesoporous structures.<sup>6–8</sup> It was reported that the capacitance value of the ordered mesoporous nickel oxide can reach as high as 590 F g<sup>-1.8</sup> It is important for ions to be transported rapidly through the porous film during high rate charging and discharging. The nickel oxide film with open macropores fabricated by polystyrene sphere template has turned out to be effective in improving the capacitance of film (351 F g<sup>-1</sup>).<sup>9</sup> The open macropores may enhance the electrolyte penetration and ion migration, therefore increasing the utilization of nickel oxide film.

The electrical conductivity also plays an important role in increasing the capacitive behavior of nickel oxide/hydroxide films. Electrodepositions of nickel hydroxides and oxides on high electronic conductivity substrates such as nickel foam,<sup>10</sup> carbon fiber,<sup>11</sup> and carbon nanotube<sup>12</sup> have shown an enhancement in their specific capacitance.

Generally, the high-rate capability of an electrode is controlled by the ion diffusion resistance within the crystal structure of active material. Diffusion resistance in the solid phase can be mitigated by shortening the diffusion path. Nickel oxide films with nanoflakes have been previously demonstrated to effectively improve the capacitive behavior of films.<sup>13,14</sup> In this work, we used a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as a template for anodic electrodeposition of nickel oxide nanoflakes with open macropores onto the stainless steel (SS) substrate. The nickel oxide films were electrodeposited directly onto the SS substrate by applying an anodic potential of 0.9 V *versus* a saturated Ag/AgCl electrode. The plating solution consisted of 0.13 M sodium acetate, 0.13 M nickel sulfate, 0.1 M sodium sulfate, and 0.001 M surfactant (CTAB) at room temperature.<sup>15</sup> After deposition, the film was rinsed several times in enthanol to remove the surfactant, and then the film was annealed at 300 °C for 1 h in air. The capacitive behavior of films was characterized using cyclic voltammetry in a three-electrode cell with 1 M KOH electrolyte. The potential was cycled at various scan rates using a potentiostat in a potential range of 0–0.45 V. The electrochemical impedance measurements were performed by means of a potentiostat which was coupled to a frequency response analyzer under the open-circuit condition.

Fig. 1 shows the TEM images of nickel oxide films after annealing at 300 °C for 1 h. The nickel oxide film deposited in the absence of CTAB possesses a compact film structure (Fig. 1a). Our previous work has demonstrated that the anodic deposited nickel oxide film is made up of flaky nickel oxide.<sup>16</sup> A compact nickel oxide film may consist of very small pores, some of which may be closed. The existence of closed pores is an important drawback because the closed pores make it difficult for electrolyte to enter into the interior of the film. Interestingly, a nickel oxide film deposited in the presence of CTAB has open macropores with a pore diameter of *ca*. 150–200 nm (Fig. 1b).

Fig. 2 shows a schematic illustration of the formation of porous nickel hydroxide films. When Ni<sup>2+</sup> ions arrive at the electrode surface via diffusion, the film formation 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 insoluble nickel oxide/hydroxide deposits on the anode substrate.<sup>16</sup> A compact film with particularly small pores is obtained by anodic deposition in absence of CTAB. When adding amphiphilic molecules (surfactants) to the plating bath. they may adsorb and desorb at the solid/solution interface depending on the applied potential. CTAB has a positively charged head group and a hydrophobic hydrocarbon chain. During anodic electrodeposition (positive potential), the positively charged head groups of CTAB may be repelled from the anode surface, while the hydrophobic chains will be attracted to the anode surface. The adsorbed CTAB may cover a part of the electrode surface and hinder the access of nickel ions to the electrode surface. Therefore, the deposited film has macropores distributed throughout the entire film.

Fig. 3a shows the cyclic voltammograms (CVs) of nickel oxide films at a scan rate of 25 mV s<sup>-1</sup>. Clearly, both films have redox peaks during the CV scan. Compared to the electrical double layer capacitance, much more capacitance

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**Fig. 1** TEM images of the nickel oxide films deposited (a) without and (b) with CTAB.



Fig. 2 Schematic illustration of the formation of porous nickel hydroxide film during electrodeposition (a) without and (b) with CTAB.



**Fig. 3** (a) CV curves of the nickel oxide films at a scan rate of 25 mV  $s^{-1}$  and (b) specific capacitance of the films at various scan rates.

can be stored in the bulk of nickel oxide by means of redox reactions. The redox couple of nickel oxide films in alkaline solution can be expressed as follows:<sup>17,18</sup>

$$NiO + OH^- \leftrightarrow NiOOH + e^-$$
 (1)

Obviously, the peak current densities of a nickel oxide film with open macropores deposited in the presence of CTAB are much higher than those of a compact film. The higher the current density, the larger is the specific capacitance of the film. The specific capacitance (C) was calculated by the equation:

$$C = \frac{1}{\nu \cdot \Delta V} \int_0^{0.45} i \cdot dV \tag{2}$$

where *i* is the current density (A  $g^{-1}$ ),  $\Delta V$  is the potential window (V), *V* is the applied potential (V), and *v* is the scan rate (V  $s^{-1}$ ). The specific capacitance of a film with open macropores at a scan rate of 25 mV  $s^{-1}$  reaches as high as 1106 F  $g^{-1}$ , which is 4.5 times higher than that of a compact film (243 F  $g^{-1}$ ). This reflects that a porous film with bigger open pores may facilitate the electrolyte transport through the film. A film with open macropores can shorten the ion migration and diffusion paths, leading to an increase in the effective surface area. While for a compact film without open macropores, the migration and diffusion resistances of ions are significantly pronounced, especially in the regions near the SS substrate.

Fig. 3b shows the effect of CV scan rate on the specific capacitance of nickel oxide films. Obviously, both films have



**Fig. 4** Nyquist plots of the nickel oxide films deposited with and without CTAB. The enlarged figure is shown in the inset of Fig. 4.

higher specific capacitance at low scan rate than those at high scan rate. A nickel oxide film with open macropores has a specific capacitance of 1110 F g<sup>-1</sup> at a low scan rate of 10 mV s<sup>-1</sup>, and the value reduces slightly to 950 F  $g^{-1}$  at a high scan rate of 200 mV s<sup>-1</sup>. A small decrease in specific capacitance with increasing scan rate indicates the high power characteristics of a nickel oxide film with open macropores. High capacitance retention at high scan rate reveals that the faradaic reaction occurring on the active sites of the nickel oxide surface is fast enough to maintain the current response during high rate scanning. Possibly, the interconnected nanoflakes provide many more paths for electron conduction, and the flake-like structure shortens the ion diffusion paths within the solid nickel oxide. More importantly, the open macropores benefit electrolyte transport and provide larger surface area for charge-transfer reactions.

Fig. 4 shows the effect of pore structure on the Nyquist plot of nickel oxide films. At very high frequencies, the intercept at real part (Z') is a combinational resistance of electrolyte resistance, intrinsic resistance of substrate, and contact resistance at the active material/current collector interface.<sup>19</sup> This value is approximately the same for both films. A major difference is the semicircle in the high-frequency range, which corresponds to the charge-transfer resistance caused by the faradaic reaction and the double-layer capacitance on the nickel oxide surface. The charge-transfer resistance of a film with open macropores was approximately 0.26  $\Omega$ , which is much lower than that of a compact film (0.57  $\Omega$ ). The charge-transfer resistance depends on the electroactive surface area of film for the faradaic reaction to occur. A film with low charge-transfer resistance is more effective for fast charge and discharge responses.<sup>20</sup> A nickel oxide film having open macropores possesses a larger electroactive surface area possibly due to an increase in the electrolyte accessible area.

In summary, nickel oxide film with nanoflakes and open macropores has been successfully prepared by anodic deposition in the presence of CTAB template. The capacitive behavior of nickel oxide film turns out to be significantly affected by the open macropores. The specific capacitance of nickel oxide film with open macropores reaches as high as 1110 F  $g^{-1}$  at a scan rate of 10 mV s<sup>-1</sup>, which is much higher than that of a compact film (254 F  $g^{-1}$ ). Possibly, a highly porous film with bigger open macropores offers large surface area for fast charge storage and redox reactions and is capable of delivering high power. The prepared nickel oxide film with open macropores also exhibits a high capacitance and a stable capacitance retention during galvanostatic cycling (see Fig. S2 in ESI†), and is therefore suitable for long-term capacitor applications in alkaline solution.

The authors gratefully acknowledge financial support from the National Science Council, Taiwan, Republic of China (Project No: NSC 98-2221-E-151-032).

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