Enhanced Pseudocapacitive Behaviour of Porous Anodic Alumina Templated Ni-Nanorod Electrodes

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Abstract

Nanostructured electrode materials with its unique structural features and increased electrochemical properties have the great potential for revolutionizing energy conversion and storage technologies. Nanostructures with distinct characteristics such as porosity, hierarchy and hollowness are extensively studied for their superior properties and their utilization in many applications such as energy storage and conversion, water treatment, sensors, and catalysts [1,2]. Their exceptional qualities particularly in energy storage devices such as batteries and supercapacitors, are primarily attributed to their large surface area and empty spaces. Supercapacitors possess several advantages over batteries, including a prolonged cycling life, a large capacity for providing power, and an environmentally friendly nature.

Pseudocapacitors are a kind of supercapacitors that store charge through oxidation and reduction reactions occurring at the surface of the electrodes. Their pseudocapacitance is a result of the rapid faradaic redox reaction [3]. In contrast, hybrid supercapacitors store charge through formation of electrical double layer at the surface. The electrode material plays an important role in energy storage applications and significantly influences the performance of the device. This work provides a comprehensive investigation of the synthesis, characterization, and electrical properties of nickel nanorod electrodes using nanoporous anodic alumina as templates for potential use in pseudocapacitor applications. The template-based synthesis approach allows for precise control over the morphology and structure, which is used to customize the electrochemical performance of the resultant electrodes.

Nanoporous anodic alumina (NAA) was fabricated by using the well-known two-step anodization technique using 0.3 M oxalic acid solution at 40 V and at 5 ºC of electrolyte temperature. To electrochemically deposit nickel, it is necessary to remove the insulating barrier layer that remains between the pores and the base aluminum after the porous material production. This barrier layer hinders the flow of current during the electrodeposition process. The step-down voltage technique was used to reduce the thickness of the barrier layer, and the remaining barrier layer was dissolved by submerging the sample in a 5 wt% phosphoric acid solution. The pulsed electrodeposition technique was employed to deposit nickel into nanopores of alumina using watts bath solution consisting of 30 g of nickel sulphate, 4.5 g of nickel chloride, and 4.5 g of boric acid dissolved in 300 ml of deionised water [4]. The experimental setup involved utilizing the NAA as the anode and platinum as counter electrode. In this technique, the current was applied in the form of constant current pulses which allows the reduction of Ni-ions and their deposition at the bottom of the pores [5]. The nickel deposited sample was immersed once again in a 5 wt% phosphoric acid solution to partially etch the walls of the pores, hence increasing the active surface area for the reaction of electrolyte ions at the nickel nanorods. The SEM characterization demonstrates the successful fabrication of nickel nanorods that are almost homogeneous in size and have well-defined dimensions and aspect ratios. Figure 1a shows the top-view of nickel deposited substrate and Fig.1b shows cross-sectional image which confirms the electrical path of Ni nanorods to the aluminium base. The estimated dimensions of these nanorods are around 65-70 nm in diameter and 2 microns in length.

In addition, the electrochemical characteristics of the nanostructured nickel nanorod electrodes were thoroughly examined using cyclic voltammetry (CV) measurements. These measurements were conducted with respect to the Ag/AgCl reference electrode and platinum as counter electrode in an electrolytic solution of 1 M KOH. The potential range is set between 0.0 and 0.8 V, and the scan rate is 50 mV/s. The fabricated electrodes exhibit notable electrochemical performance due to their large surface area-to-volume ratio and effective charge transfer kinetics. CV of the Ni nanorods sample after 500th cycles is shown in Fig 2a. The curve shows well defined redox peaks that indicate better stability and reversibility. This highlights the enhanced electrochemical activity and durability of the nanostructured electrodes. These peaks correspond to the pseudocapacitance characteristics of the material and are distinct from the behavior of double layer capacitance. The formation of these peaks is a consequence of the oxidation and reduction reaction that occurs between the electrolyte and the active substance. The redox reaction occurring at the nanorods surfaces is:

$$Ni + 2OH^- \leftrightarrow Ni(OH)_2 + e^-$$

The specific capacitance of the electrode was calculated to be approx. 102 Fcm^{-2}. Fig. 2b shows the plot of the specific capacitance as a function of the number of cycles. The plot shows the specific capacitance is reduced by only 18% after 1000 cycles., indicating a favorable retention capacity. It has also been noted that with increasing number of cycles the shape of the CV was not distorted, and it maintained the pseudocapacitive behaviour even after long number of cycles which is essential for long lifespan working of electrodes in energy storage devices applications.

In this study we have extensively investigated the impact of important factors such as effect of nanostructuring of the metals, nanorod size, electrolyte composition, and scan rate on the electrochemical characteristics. The aim is to understand the fundamental mechanisms that control the performance of the nanostructured electrodes. The results highlight the importance of nanostructuring in improving the electrochemical characteristics of nickel-based electrodes for different energy storage and conversion purposes, indicating their potential for practical implementation in next-generation energy technologies.

References

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Figures

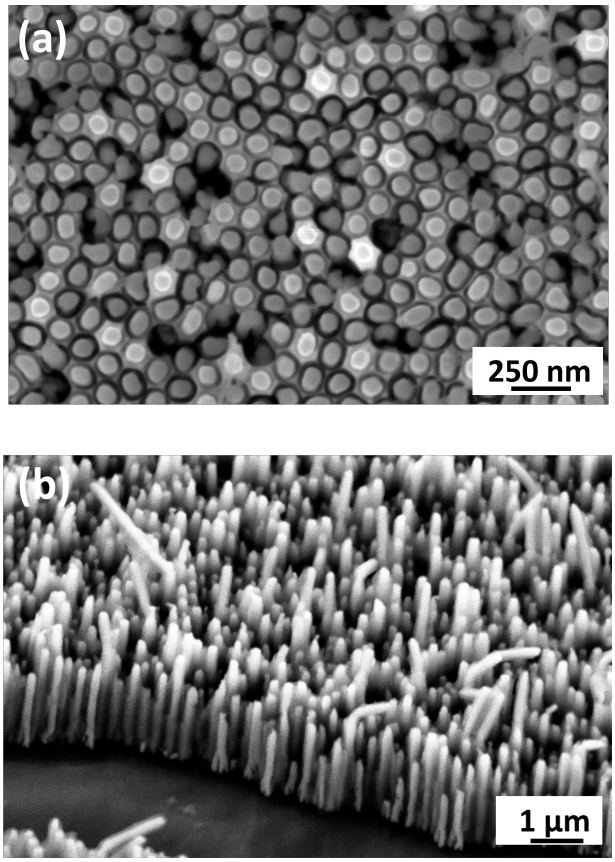

Figure 1. FESEM images (a) top view of nickel nanorods deposited within the pores of alumina, and (b) cross sectional view of nickel nanorods attached with the base aluminium.

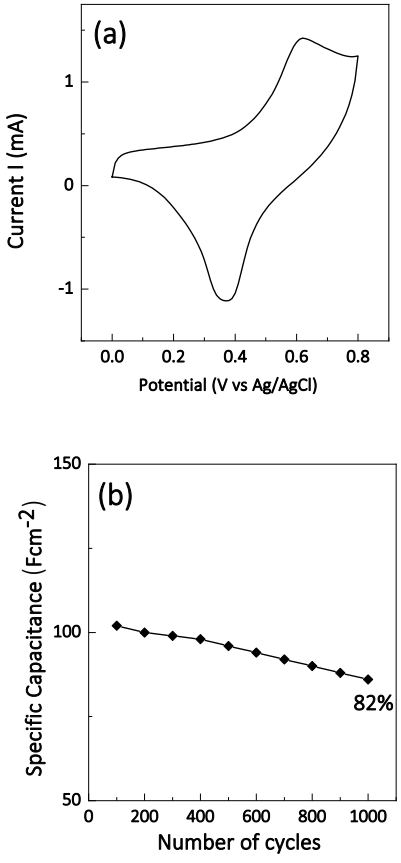

Figure 2. Cyclic voltammetry curves (a) CV at 500th cycle of Ni nanorods electrode with reference to Ag/AgCl electrode, and (b) specific capacitance vs number of cycles graph stating the retention capacity.