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Article

# Development of Nanoporous Nickel Oxide Materials as Electrodes for Supercapacitors

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**Abstract:** As a potential electrochemical energy storage device, supercapacitor has been researched owing to its low weight, excellent power density, outstanding charging rate, and long durability. For the supercapacitor, the electrode material and its morphology determine its overall performance. Nickel oxide (NiO) is a promising material for the electrode because of its low cost, high specific capacitance, and eco-friendly manufacturing process. In this research, we developed a simple and cost-effective method to fabricate supercapacitor electrodes by electrospinning and thermal annealing, making porous nickel oxide nanofibers directly grow on 3D-nickel foam. The binder-free design and porous structure of electrodes enhance the ion transport and electron transfer in the supercapacitor. The crystal structure of NiO was identified by X-ray diffractometry (XRD). The morphological and microstructural characterization was analyzed by scanning electron microscopy (SEM). The electrochemical test was carried out in a three-electrode electrochemical cell with the obtained foamed NiO as the working electrode, the platinum sheet as the counter electrode, and the Ag/Cl electrode as the reference electrode. The electrochemical performance was evaluated by using cyclic voltammetry (CV), galvanostatic charge/discharge technique, and electrochemical impedance spectroscopy (EIS). Due to the large specific surface area and good electrical conductivity of the NiO electrode, the supercapacitor exhibited excellent electrochemical performance (591 F/g at 2 A/g). After 1500 cycles of charging and discharging at 10 A/g, the capacitance of the supercapacitor using the NiO electrode increased by 21.7% with excellent cycle stability.

**Keywords:** Supercapacitor, Nickel oxide, Electrospinning, Binder-free electrode, Nanoporous

## 1. Introduction

Supercapacitors are characterized by high power density (>10 kW/kg), low cost, extended cycle life (>1 million cycles), high energy conversion efficiency (over 90% cycling efficiency at high currents), high safety factor (long-term use with minimal maintenance), and excellent low-temperature performance (stable operation at −30°C). They are considered promising candidates for future energy storage. Supercapacitors can be applied to large industrial equipment, memory backup devices, renewable energy power plants, and electric or hybrid electric vehicles or electrified trains [1]. Transition metal oxides with high theoretical capacitance have been investigated as electrode materials for supercapacitors to enhance the specific capacitance and energy density of supercapacitors.

Ruthenium oxide ($RuO_2$), iridium oxide ($IrO_2$), manganese oxide ($MnO_2$), cobalt oxide ($Co_3O_4$), nickel oxide (NiO), tin oxide ($SnO_2$), iron oxide ($Fe_2O_3$), vanadium oxide ($V_2O_5$), copper oxide (CuO), tungsten oxide ($WO_3$), perovskite, molybdenum oxide ($MoO_3$), and iron oxide belong to transition metal oxides. Among them, $RuO_2$ is considered the most active electrode material but its inherent toxicity and high cost in production limit its application. Thus, nickel oxide (NiO) has been paid much attention to replace $RuO_2$ [1] and is widely applied in supercapacitors. NiO shows high theoretical capacitance (2573 F/g in a potential window of 0.5 V), high thermal and chemical stability, low price, and easy affordability with an eco-friendly manufacturing process [3]. However, recent studies indicate that its specific capacitance and cycling capability are relatively poor due to poor conductivity, insufficient redox-active sites, and an unstable charge-discharge process [4]. However, the fabrication of NiO electrodes in the nanoscale can enhance their surface area to solve these problems [5]. We developed NiO electrodes in this research using a cost-effective electrospinning technique to produce NiO nanofibers to take advantage of their properties. As the nanofibers are directly grown on nickel foam, resulting binder-free electrodes showed low internal resistance and outstanding specific capacitance.

## 2. Method

The polymeric solution for electrospinning was prepared by dissolving $Ni(CH_3COO)_2 \cdot 4H_2O$, 6.1 g of $C_6H_8O_7 \cdot H_2O$, and 2.0 g of polyvinylpyrrolidone (PVP) in 5 mL of deionized water. Then, the solution was heated to 80°C with constant stirring until its color turned into transparent green as shown in Fig. 1a. Subsequently, the precursor solution was loaded into a syringe mounted on the pump for electrospinning. Electrospinning was performed at a high voltage of 25 kV with a flow rate of 0.2 mL/h. The spun nanofibers (NFs) were collected on a piece of Ni foam which was placed 20 cm away from the tip of the nozzle (Fig. 1b). The Ni foam-supported NFs were then put into a tube furnace, heated in high-purity nitrogen to 500 °C (Fig. 1c), and maintained for 2 h until NiO was to crystallized and NFs were adhered to the Ni foam.

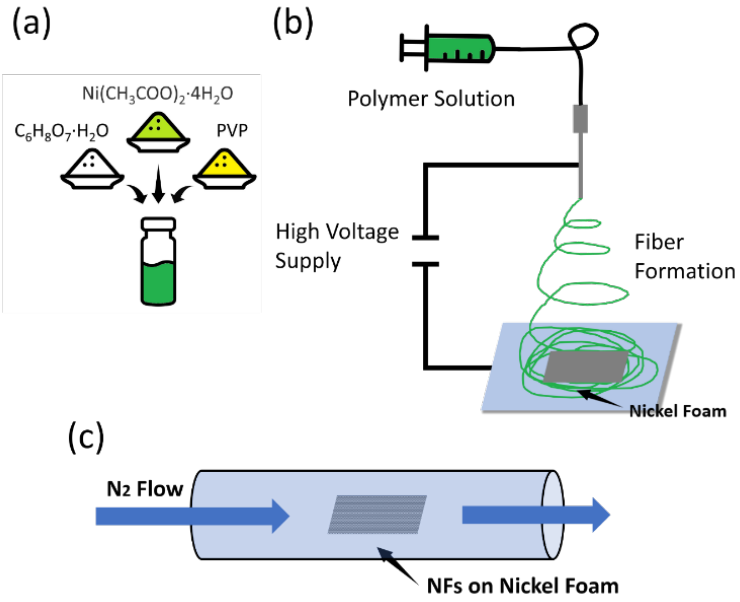


**Fig. 1.** Schematics of (**a**) the polymeric solution, (**b**) electrospinning set-up, and (**c**) annealing process in a tube furnace.

The crystal structure of the NiO-NFs was identified by X-ray diffractometry (XRD). The morphological and microstructural characterization was carried out by using scanning electron microscopy (SEM). The electrochemical tests were conducted in a three-electrode electrochemical cell with the as-obtained Ni-NFs/Ni as a binder-free working electrode, a platinum flake as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The electrochemical performance was evaluated galvanostatic charge/discharge technique using cyclic voltammetry (CV). All the tests were conducted at room temperature using 2 M KOH aqueous solution.

## 3. Results and Discussion

Fig. 2a shows that the average diameter of NiO-NFs was 280–400 nm, and NiO-NFs were highly porous. Figs. 2b,c present the interconnected network of fiber-like structures on the whole surface, indicating that this foam was porous with a high surface area. The NFs were spun on the substrate densely and evenly (Fig. 2d). The XRD pattern of the as-fabricated NiO-NFs/Ni electrodes showed the diffraction peaks at 37.31, 43.31, and 62.91° which were perfectly assigned to the diffractions from (111), (200), and (220) crystal planes of cubic NiO (JCPDS 075-0197) (Fig. 3), while the peaks were found at 44.61,51.91 and 76.41° in the underlying Ni foam. The energy-dispersive X-ray (EDX) spectrum confirmed the composition of the NFs consisting of Ni and O. The Si peak from the silicon substrate and Pt peak originated from the SEM contamination (Fig. 4). The NiO-NFs/Ni composite was fabricated as a binder-free electrode to examine its electrochemical properties. Fig. 5a shows the cyclic voltammetry (CV) curves of the electrode scan at various scan rates and distinct redox peaks. These peaks indicated that the electrode capacitance was influenced by the interfacial redox reaction: $NiO + OH^- \rightarrow 2NiOOH + e^-$ [6].

The redox peak positions remained constant despite changes in the scan rate, indicating rapid ionic and electronic transportation even at a high scan rate of 100 $mVs^{-1}$. The porous structure of NiO-NFs and the binder-free structure facilitated the effective transport and collection of charges for these phenomena. The galvanic charge/discharge profiles of the binder-free NiO-NFs/Ni electrodes are presented in Fig. 5. The pseudo-capacitive nature of the electrode was confirmed by the non-linear characteristics of

the charge/discharge curves for all current densities, which was consistent with the findings from cyclic voltammetry (CV). The surface redox reaction occurred with a gradual variation in the potential between 0.35 and 0.45 V, which has a significant impact on the overall capacitance. The double-layer capacitance contributed minimally to the electrode's overall capacitance which was indicated by the rapid linear change in potential in the range of 0–0.35 V. The specific capacitance was 591 F/g at a current density of 2 A/g. At a current density of 8 A/g, 87% of capacitance was maintained after 1500 cycles. Fig. 5c shows that the NiO-NFs/Ni electrode maintained its stability at 3A/g for 1500 cycles with a degradation reate of 13%.

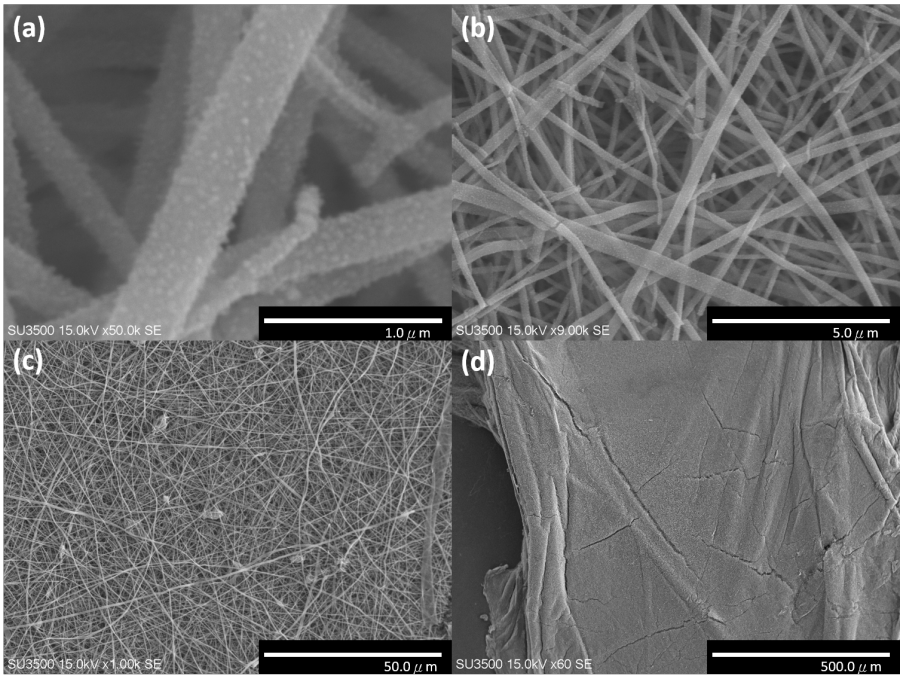


**Fig. 2.** Morphology of electrospun porous Ni-NFs on Ni foam was observed through SEM magnified by (**a**) 50,000, (**b**) 90,000, (**c**) 100,000, and (**d**) 600,000.

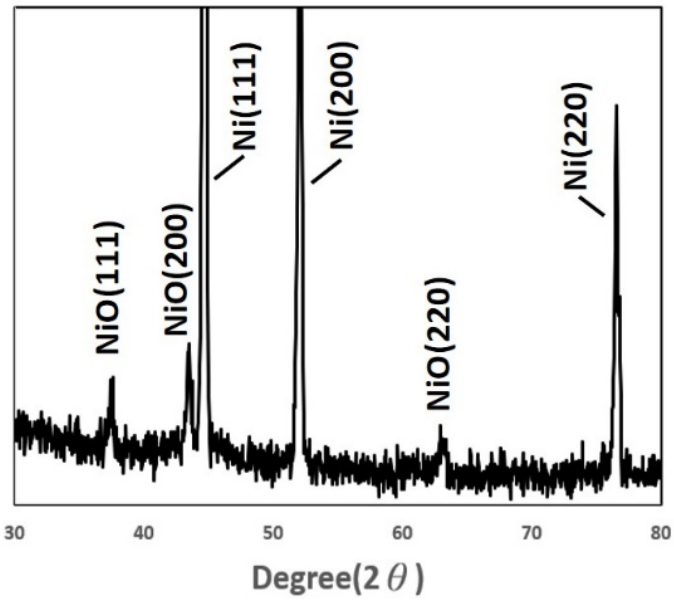


**Fig. 3.** XRD pattern of binder-free porous NiO-NF fibers.

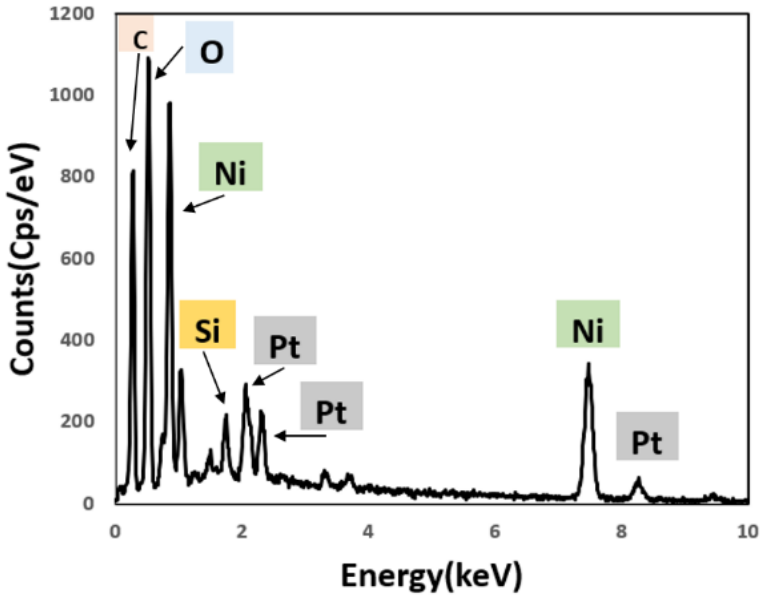


**Fig. 4.** EDX spectrum of binder-free porous NiO-NF fibers.

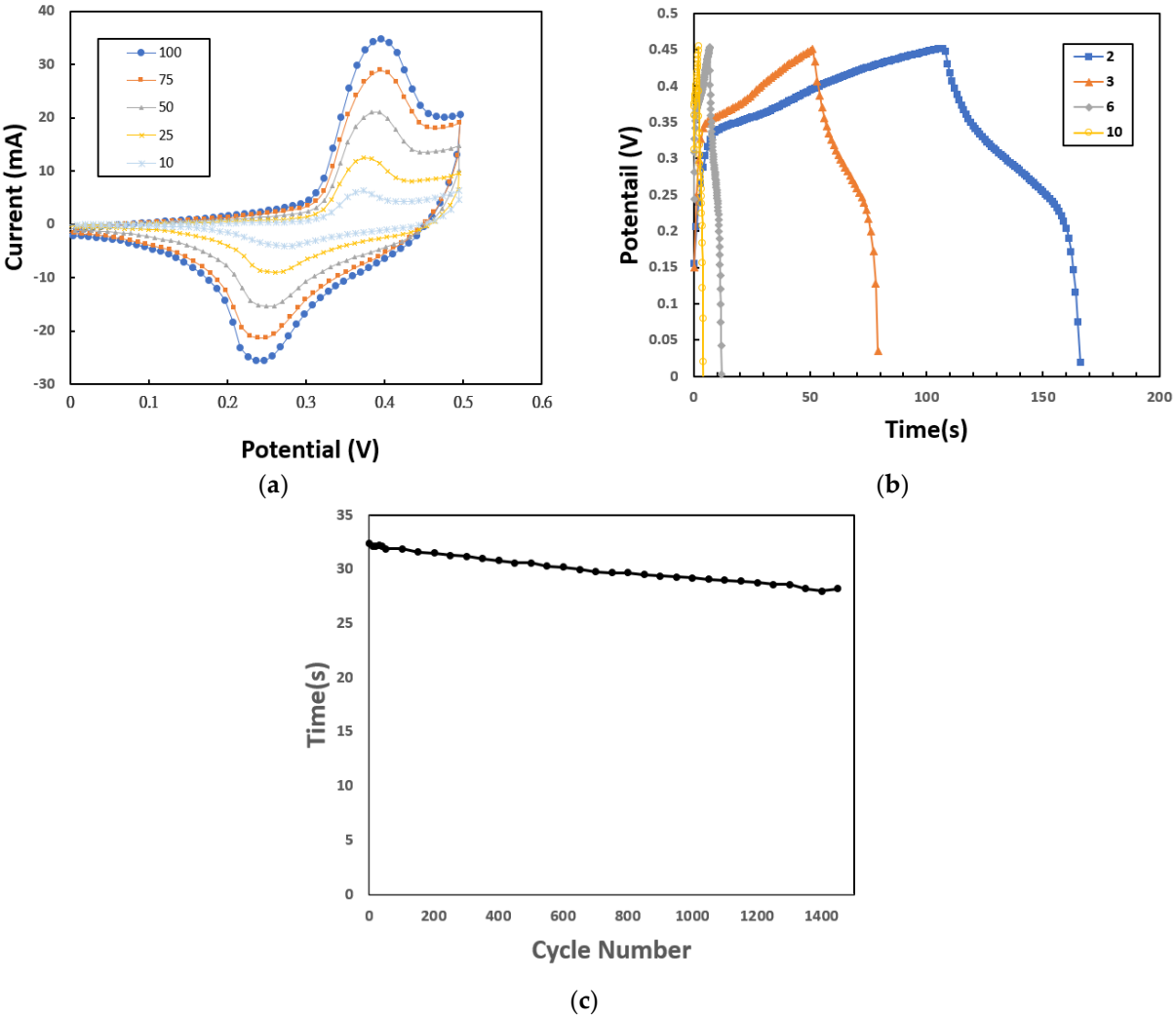


**Fig. 5.** (**a**) Cyclic voltammetry, (**b**) galvanostatic charge/discharge, and (**c**) cycling performance of fabricated Ni-NFs.

## 4. Conclusion

In this study, binder-free electrodes consisting of porous NiO nanofibers were directly electrospun on a Ni foam. The obtained Ni-NF showed a high specific capacitance of 591 F/g at a current density of 2 A/g and a stability of 87% after 1500 cycles, The fabricated electrode is an excellent candidate for supercapacitors which can be used for large industrial equipment, memory backup devices, renewable energy power plants, and electric or hybrid electric vehicles or electrified trains.

**Author Contributions:** Y.-M. Lu. is responsible for the experiment planning, directing the research content, and writing this paper. Y.-C. Lin and T.-Y. Liu are responsible for some experiments and data sorting. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data of this study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The authors declare no conflict of interest.

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