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RESEARCH

Molybdate composite based nickel and bismuth anchored on multi-walled carbon nanotubes as efficient electrodes for asymmetric supercapacitor applications

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Abstract

For advanced supercapacitor applications, this work presents the synthesis of an electrochemical investigations of nickel and bismuth molybdate blended with multi-walled carbon nanotubes (MWCNTs). We have adopted simple sol-gel procedure for synthesis of nanostructures. Structural, textural and morphological analysis indicates the presence of high purity and advantageous porous morphology. The electrochemical analysis of both samples shows the specific capacitance of 728 Fg^{-1} for Nickel Molybdate with Carbon Nanotubes (NM@CNT) and 542 Fg^{-1} for Bismuth Molybdate with Carbon Nanotubes (BM@CNT) nanocomposites. NM@CNT stood out for its better energy density and power density as a full cell (26.5 $Whkg^{-1}$ at 2517 Wkg^{-1}). By facilitating improved ionic transport, electrochemical kinetics, and charge retention, metal molybdates and MWCNTs work in concert to position NM@CNT for energy-focused devices and BM@CNT for power-intensive supercapacitor applications.

Keywords Nickel-bismuth molybdates · Supercapacitor · Metal molybdate electrodes · Specific capacitance

Introduction

Energy crisis is a significant aspect that can have a profound impact on the world economy. The increasing population has as direct impact on the energy resource in terms of advancing technology. It is also difficult to meet the requirements by only using the conventional energy sources. Hence alternative energy storage system is being investigated and explored by many research teams. One among those treasured system is the supercapacitor, which bridges the gap between conventional capacitors because of its increased power efficiency, stability, longevity, and quick charging and discharging. However, it is difficult to meet these requirements using only conventional energy sources. In particular, supercapacitors specifically face critical bottlenecks such as, EDLC carbon electrodes limited to ~250 Fg^{-1} with low energy density, pseudocapacitive metal oxides with poor electrical conductivity and particle aggregation restricting ion diffusion, narrow operating voltage windows (~1.0 V) limiting energy density ($E \propto V^2$), and complex asymmetric device fabrication with charge balancing challenges, and many existing energy-storage devices still suffer from limited rate capability, and insufficient cycling stability [1]. In particular, conventional EDLC-type carbon electrodes offer excellent power and long life but store relatively low energy, whereas battery-type materials provide higher energy density but often exhibit sluggish redox kinetics and structural degradation during long-term cycling. Hence, alternative energy-storage systems and new electrode architectures are being investigated and explored by many researchers. Materials like nickel and bismuth molybdate doped CNTs have attracted interest in energy storage due to their redox mechanisms and ability to facilitate pseudocapacitive charge-storage processes. Nickel molybdate ($NiMoO_4$) is known for its good electrical conductivity and high capacitance,

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while bismuth molybdate (Bi_2MoO_4) delivers excellent cycling stability, making both promising candidates for pseudocapacitive energy storage in supercapacitors. When these metal molybdates (AxMoOy) are integrated with multi-walled carbon nanotubes (MWCNTs), the conductive CNT network can mitigate the intrinsic conductivity limitations of the oxides, provide additional double-layer capacitance, and increase the number of electrochemically accessible active sites [2]. Therefore, the development of $NiMoO_4$@MWCNT and $BiMoO_4$@MWCNT electrodes is important to simultaneously enhance energy density, power density, and cycling stability compared to using either metal molybdates or carbon alone. With metal molybdates and MWCNTs, supercapacitors with double-layer mechanisms and pseudocapacitance behavior can store more energy than a traditional capacitor [3]. In Nickel-bismuth composite with MWCNTs the importance of electrolyte is also essential for maximizing ion transport, charge transfer, stability, and catalytic activity for electrochemical energy storage. Proper electrolyte selection improves ion accessibility to redox-active sites, lowers impedance, and enables fast charge-storage processes required for high-power applications. The interaction between electrolyte ions and electrode surfaces directly affects device efficiency and durability [4]. Nickel (Ni) and Bismuth (Bi) is one of the most valuable metals found in the Earth's crust. Nickel serves as a transition metal, because of its intriguing properties like, low toxicity and environmental friendliness, they are regarded as a good option for energy storage. Whereas Bismuth is a P-block element which plays a key role in energy storage due to its better specific capacitance and enhanced energy density. Bismuth also synergize with transition metals like Ni in molybdates and improve their stability. Sol-gel method was found to be an effective route for synthesizing nickel and bismuth molybdate/carbon composites. These composites were prepared at a temperature of 650 ^{o}C and were subjected to electrochemical analysis. Ayman S.Eliwa investigated the nickel metal-organic framework-based surfaces for effective supercapacitor application and achieved a specific capacitance of 402 Fg^{-1} at 1 $mAcm^{-2}$ over 1000 cycles of stability at 5 Ag^{-1} [5]. Though most of the reported studies shows supercapacitor applications of a single material, this study provides a correlative analysis of Nickel and Bismuth as electrode materials for supercapacitor applications. An aqueous KOH electrolyte was used in this work because of its broad working temperature range, and capacity to promote quick and reversible redox reactions on electrode surfaces based on nickel and bismuth, which improves rate capability and cycling stability [6].

The choice of $NiMoO_4$@CNT and $BiMoO_4$@CNT as promising pseudocapacitive electrodes is that, transition-metal molybdates provide several accessible redox states, a relatively high theoretical capacity, and strong oxide frameworks appropriate for quick, reversible charge storage in alkaline electrolytes [7]. Hence, nickel molybdate ($NiMoO_4$) and bismuth molybdate ($BiMoO_4$) are appealing positive electrode materials for supercapacitors. By combining $NiMoO_4$ and $BiMoO_4$ with multi-walled carbon nanotubes (MWCNTs), a conductive, mechanically flexible three-dimensional scaffold is created that shortens electron-transport pathways, increases electric double-layer capacitance, and aids in dispersing the active particles to reveal more electrochemically accessible sites [8]. In particular, our study depicts a systematic assessment of $NiMoO_4$@CNT and $BiMoO_4$@CNT composites effect on structure, charge storage mechanism, and device performance based on their synthesised temperature conditions. Although $NiMoO_4$@CNT and $BiMoO_4$@CNT composites have been described before, this work identifies certain crucial differences. First, under identical synthesis, characterisation, and device testing conditions, this is the first systematic comparison of $NiMoO_4$@CNT and $BiMoO_4$@CNT. Second, unlike traditional hydrothermal approaches that result in aggregated nanoparticles, our novel citrate-mediated sol-gel synthesis yields distinctively hierarchical $NiMoO_4$ nanoflakes (15–25 nm) uniformly anchored along MWCNT networks. Lastly, the quantitative Dunn's analysis reveals different charge storage mechanisms like BM@CNT displays surface-dominated pseudocapacitance, allowing superior power delivery, whereas NM@CNT displays balanced hybrid behaviour, optimising energy-power applications [9].

In overall, this study emphasises the testing of structural, morphological and electrochemical properties of bismuth and nickel molybdate with CNT. The physical and chemical properties of the materials were confirmed using various analytical characterization techniques. Additionally, they were subjected to analyse ASC device applications. In comparison, nickel molybdate@CNT provides a high energy density, while bismuth molybdate@CNT is better suited for high-power and quick charge/discharge applications.

Experimental section

Materials

The chemical precursors used in the synthesis process was Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O \geq 99.9\%$), Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O \geq 98\%$), Ammonium hepta molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O \geq 99.0\%$), Multi-walled carbon nanotubes (MWCNT functionalized powder, L/D ~ 1000, ≥ 99.9 wt %), Citric acid monohydrate (HOC(COOH)

542 Fg^{-1} at 1 Ag^{-1} for NM@CNT and BM@CNT, respectively, underscoring their robust charge storage capability. NM@CNT prioritizes energy storage by achieving energy density of 26.5 Wh kg^{-1} at a power density of 2517.5 W kg^{-1}, which is higher than the BM@CNT sample. The ASC device based on NM@CNT revealed a better energy density (297 Fg^{-1}, 41 Wh kg^{-1}). These findings position NM@CNT as a candidate for energy-oriented devices and BM@CNT for power-intensive applications.

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Data availability Data sets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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