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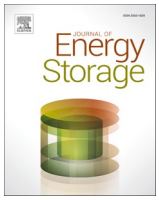

Research papers

Synergistic hybrid charge-storage mechanisms in hierarchical Ni-intercalated $Co_3(PO_4)_2.8H_2O$@$NiCoSe_2$ heterostructures for high-energy aqueous supercapatteries

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ABSTRACT

The development of next-generation aqueous supercapatteries with high energy and long life remains impeded by traditional redox-active electrode materials, which exhibit slow redox kinetics and low conductivity. In this work, a rationally designed Ni-$Co_3(PO_4)_2.8H_2O$@$NiCoSe_2$ (NCP@NCSe) heterostructure electrode is reported for energy storage applications. As a positive electrode for supercapacitors, the heterostructure offers synergistic interfacial charge-storage mechanisms and enhanced structural durability. The assembled NCP@NCSe||AC (Activated Carbon) device exhibits an outstanding specific capacity of 251.7 mAh g^{-1}, a high energy density of 68.5 Wh kg^{-1}, and a reasonable power density of 272.2 W kg^{-1} at a current density of 1 mA g^{-1}. The heterostructured interface between different materials exposes inaccessible Co redox sites, thereby increasing charge-storage efficiency. Hence, the supercapattery delivers a significant energy density with a reasonable power density and, at the same time, exhibits excellent cycling durability with 88% capacity retention after 5000 cycles. The collective enhancements clearly indicate that heterostructure engineering is an effective method for getting a well-balanced trade-off between energy and power density in aqueous supercapatteries.

1. Introduction

Supercapattery is an emerging hybrid energy storage technology characterized by high energy and power density, long cycle life, and potential for sustainable energy solutions. Redox-based electrode materials are gaining popularity as a means to make supercapatteries competitive in terms of specific capacity, energy, and power output. Consequently, a wide range of positive electrode materials has been researched for supercapatteries to enhance the device's energy density. Transition metal oxides such as NiO, Co_3O_4, $NiCo_2O_4$, MnO_2, RuO_2, and V_2O_5 are extensively studied as positive electrodes (i.e., battery-type electrodes) in supercapatteries [1,2]. These materials demonstrate success through their exceptional specific capacity, including both volumetric and areal capacity enhancement, and their sustained performance over extended periods, resulting from their low active mass loading, which remains below 3 mg cm^{-2}. The specific capacity values decrease sharply as active mass loading or electrode thickness increases, because thicker materials provide limited surface access for ions and exhibit poor electrical conductivity [3]. The device's actual metric performance under heavy mass-loading conditions poses a recurring challenge for maintaining a balance between gravimetric and volumetric capacities in battery-like pseudocapacitive materials [4]. The ability of nanostructures fabricated on conductive surfaces to enhance ion movement has been demonstrated [5]. However, the high mass loading on the metal current collector led to sluggish ion transport/or charge transfer in the electrode. Therefore, to achieve actual metric-specific capacity at high mass loading, a rational design of heterostructured electrodes, combined with controlled interfacial synthesis, is required to boost ion/electron transport and maximize electroactive surface area for enhanced electrochemical performance. Recently, metal phosphates, especially transition metal phosphates (TMPs), have attracted attention for their remarkable electrochemical activity, multivalence, strong redox properties, chemical stability, and high electrical capacitance [6]. The stable phosphate framework in TMPs improves their structural

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stability during continuous charge-discharge cycles. The non-metallic, multivalent phosphorus provides more conduction pathways for transition-metal ions, thereby increasing electrical conductivity [7]. Therefore, researchers are exploring transition-metal phosphates as promising positive electrode materials for supercapatteries. The potential transition-metal phosphates, including Ni, Co, Cu, Mn, and V, have been studied thus far. One among them, Co has received more attention because it generates a strong bonding with (PO_4), forms a stable $CoPO_4$ structure, and offers excellent physicochemical stability. Additionally, the low cost and non-toxic nature of $CoPO_4$ provides added advantages [8], towards sustainability [9,10]. Nevertheless, $CoPO_4$-based supercapatteries are further hindered by limited energy density and rate capability owing to low intrinsic conductivity and limited surface area [7,11]. Consequently, the design and engineering of the $CoPO_4$ structure are necessary to enable its use in practical applications. Rational design of $CoPO_4$ heterostructures by integrating with other conductive phases, such as metal oxides (e.g., $NiCo_2O_4$, MnO_2, etc.) or composites with different carbonaceous materials, provides synergistic redox contributions from various components, increases surface area, and electrical conductivity. As a result, this significantly improves the device's rate performance and energy density.

Hetero-nanostructure assembly on conducting substrates is considered a new strategy to improve the electrochemical activity of materials for supercapatteries [6]. Furthermore, the development of heterostructures including distinct phase materials improves structural stability, active surface area, and Faradic redox reactions [12]. Several heterostructure combinations have been reported, including $NiMoO_4$-$CoPO_4$ [13], $Co_3(PO_4)_2$/GO [7], Ni/$CoPO_4$ [14], NiCu-PO_x/NGQDs [15], Co_3O_4-$Co_3(PO_4)_2$ [16], and $Fe_{0.4}Co_{0.6}Se_2$@NiCo-P [17]. These results reveal that the desired heterostructure electrode materials perform better electrochemically than the individual components. Bimetallic $NiCoSe_2$ possesses good electrical conductivity and strong covalent coupling, making it a viable electrode for energy storage applications. Furthermore, Se's higher atomic radius and interlayer distance create more redox-active sites. Hou et al. created a two-step solvothermal $NiCoSe_2$ hollow microsphere-based energy storage device with a specific energy density of 35 Wh kg^{-1} and 82% capacity retention [18]. Binder-free $CoNiSe_2$ nanorods on nickel foam delivered an energy of 50.66 Wh kg^{-1} with long-term stability of 10,000 cycles [19]. In a recent study, NiCoSe grown on carbon cloth using a hydrothermal technique showed specific energy and power of 28 Wh kg^{-1} and 646 W kg^{-1}, respectively, with 85% capacity retention after 5000 cycles [20]. The main drawback of selenide-based electrode systems is poor cycling and a limited surface area [21]. To address these challenges, a heterostructure composed of many metals could significantly increase their performance [22]. However, it remains difficult to synthesize heterostructure materials directly on a conducting substrate.

Besides, the charge-storage mechanism of the heterostructure electrode is complex, particularly in transition-metal compounds, owing to the involvement of multiple redox processes. It can be associated with the underpotential deposition, the Faradaic surface redox process, and the intercalation into the bulk lattice [23]. Heterostructures or composite materials exhibit a coupled charge–storage mechanism and show enhanced power and energy density [24]. Generally, Faradaic redox features are a popular charge-storage mechanism, applied to various electrode materials, including metal oxides, phosphates, selenides, and their heterostructures [20,25–27]. Among them, the combination of a surface Faradaic reaction with bulk intercalation is rarely reported [28]. In this case, both the intercalation of ions into the tunnels or layers of redox-active materials and rapid Faradaic charge transfer occur without a change in crystalline phase [29]. Consequently, this coupled surface Faradaic and intercalation storage mechanism leads to a higher rate capability than that of battery-type materials, which depend solely on intercalation. The emergence of an intercalation-type charge-storage mechanism in electrodes results in a high energy density for the device. Only a few crystalline materials have a unique structure that can accommodate fast ion transport into the bulk lattice [30]. Therefore, rational design of an electrode with ion intercalation and fast ion transfer kinetics is promising for the fabrication of next-generation supercapatteries to deliver stable energy and power densities.

Transition metal selenides (e.g., $NiSe_2$, $CoSe_2$, $NiCoSe_2$) coupled with TMPs show excellent specific capacity because of their distinctive heterostructure. A $CoNiSe_2$/NC@$Ni_3(PO_4)_2$ heterostructure with an open space exhibits a high specific capacitance of 2505 F g^{-1} and outstanding cycle stability [31]. Similarly, electrodeposited FeCo-Se@NiCo-PO_4 has a charge storage capacity of 888.6C g^{-1} (2221.5 F g^{-1}) at 1 A g^{-1} and 98% coulombic efficiency [32]. Wan et al. reported that a free-standing $Fe_{0.4}Co_{0.6}Se_2$@NiCo-P and $Co_{0.7}Fe_{0.3}Se_2$@NiCoPO heteroarchitecture on a carbon cloth substrate demonstrates a gravimetric capacity of 202.3 mAh g^{-1} and 887.4C g^{-1} at 1 A g^{-1} and good cyclic stability over 5000 cycles [17,33]. They showed distinct electrochemical performance by varying the composition of metallic selenides. However, the mechanistic insights into the charge-storage mechanism are unclear. Also, the energy and power densities of these materials must be increased to compete with lithium-ion batteries. Supriya et al. [28] studied a tunable charge-storage mechanism in an electrodeposited nickel-cobalt phosphate thin film. It reports a coupled surface Faradaic and intercalation-type charge-storage mechanism in the NCP@NCSe heterostructure to improve the device's energy density. To date, various methods for fabricating heterostructures have been developed, including chemical precipitation, hydrothermal synthesis, electrodeposition, and so on [16,32,34]. A combination of hydrothermal and electrodeposition techniques could be helpful for rational heterostructure design. In this study, we synthesized the NCP@NCSe heterostructure as a positive electrode for a supercapattery. A two-step procedure combining hydrothermal and electrodeposition to produce the NCP@NCSe heterostructure and examine its potential for energy storage applications. The heterostructure of NCP@NCSe exhibits excellent electrochemical properties compared to pristine CP, owing to the synergistic effect of the redox-active phosphate and conductive selenide. The layered hetero-architecture showed an exceptional specific capacity of 251 mAh g^{-1} at 1 mA g^{-1}, and the supercapattery achieved an energy density of 68.5 Wh kg^{1} and a reasonable power density of 272.2 W kg^{1}, along with long-term durability over 5000 cycles. The facilitated kinetics are associated with a hybrid charge-storage mechanism involving $NiCoSe_2$ and hydrated phosphate, which provides ample electroactive sites and structural stability.

2. Experimental procedures

2.1. Materials and methods

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), Nickel Nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), Ammonium dihydrogen phosphate ($NH_4H_2PO_4$), Urea (CH_4N_2O), and Selenium dioxide (SeO_2) are purchased from Sigma Aldrich and used as received without further processing. Ultra-pure nickel foam (99.99%, 80–120 pores per inch with 1 mm thick) purchased from Fuel Cell Store, USA.

2.2. Synthesis of $Co_3(PO_4)_2{\cdot}8H_2O$

To synthesize $Co_3(PO_4)_2{\cdot}8H_2O$ (CP), a 10 mM solution of $Co(NO_3)_2{\cdot}6H_2O$ dissolved in 40 ml of polyethylene glycol [PEG], and an equal mole ratio (10 mM) of $NH_4H_2PO_4$ was dissolved in 40 ml of DI water under constant stirring. The clear phosphate solution was added dropwise to the cobalt metal solution, and the mixture was stirred continuously for 30 min. Once the ionic exchange reaction was completed, 1 M of CH_4N_2O was added to the mixed solution. The mixture was transferred to a Teflon-coated stainless-steel autoclave containing the pretreated nickel foam and heated in an oven for 8 h at 160 °C. Finally, the oven naturally cooled to room temperature, and the CP- grown NF was removed. The sample was washed with ethanol and

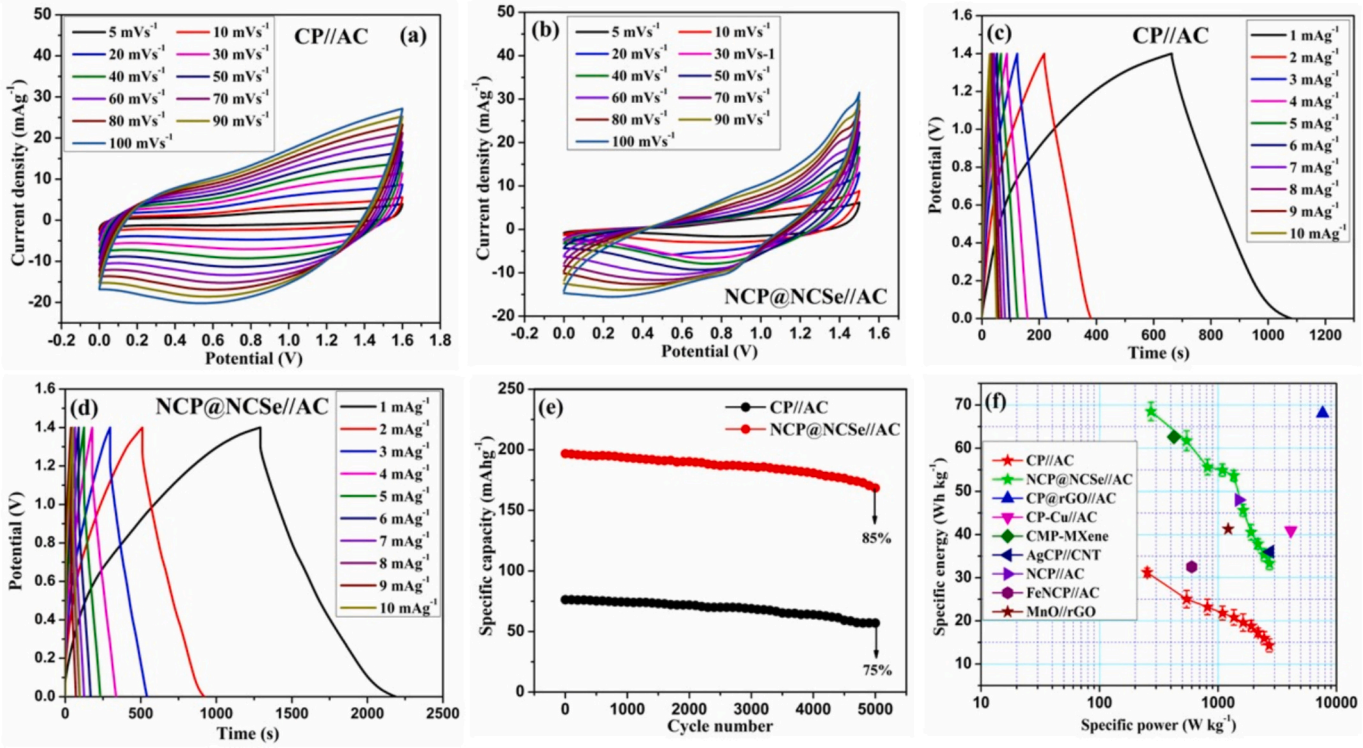

Fig. 9. (a & b) CV and (c & d) GCD characteristics of the Cp//AC and NCP@NCSe//AC supercapatteries measured using a two-electrode configuration. (e) The cyclic stability of the devices measured at 5 mAg^{-1} and (f) The Ragone plot for the devices compared with recent publications.

partial fragmentation was observed (Fig. S14b). A HRTEM image (Fig. S14c) with clear lattice fringes demonstrating the retained crystallinity. The outer region with a defined lattice fringe of the hydroxide phase suggests surface reconstruction. The observed SAED pattern in Fig. S14(d), with a diffuse ring and discrete diffraction spots, indicates the formation of a mixed crystalline-amorphous phase after 5000 cycles. The presence of conductive secondary phases forms low-resistance electron pathways, while porous or layered materials facilitate rapid ion diffusion. The energy and power densities are important factors in utilizing materials for real device applications. The Ragone plot of the calculated energy and power output of both devices is depicted in Fig. 9f, and the values are presented in Table S1. The energy density of the NCP@NCSe//AC device doubled when compared to CP//AC. The heterostructure-based device delivers a maximum energy density of 68.5 Wh kg^{-1}, whereas the pristine one exhibits 31.2 Wh kg^{-1} with the power output of 272.2 and 252.5 W kg^{-1} at 1 mAg^{-1}, respectively. At the same time, the energy density was maintained at 33.3 W kg^{-1}, even at a high current density of 10 mAg^{-1}, for the heterostructure-based device. As shown in the Ragone plot, the heterostructure device exhibits a large energy output and a stable power density as the current density increases. The close contact between the different materials at the interface promotes surface redox reactions, facilitates ion transport to the active sites, and allows the electrolyte to penetrate deeper. This leads to a substantial increase in charge-storage capacity, which directly elevates the energy density. On the other hand, both devices deliver the same order of power output. Interfacial engineering has reduced charge-transfer resistance, though the inherent limitations of ionic diffusivity in battery-type materials, along with the composite's fair electrical conductivity, still limit the rate capability to moderate levels. Moreover, increased active-mass loading, which is often necessary to achieve higher energy density, can counterbalance the improvement in electronic transport. As a result, the device shows a significantly higher energy density, while the power density remains largely unchanged. The proposed heterostructures remarkably increase the energy density due to their structural characteristics—enlarged electroactive interfaces, hierarchical porosity, coexisting charge-storage mechanisms, and improved electrical pathways—that enhance the total charge per cycle. However, the intrinsic kinetic limitations of hetero-phase materials, a slight increase in bulk conductivity, and a constant equivalent series resistance limit the increase in power density. Therefore, in our NCP@NCSe//AC device, although the energy density is doubled, the power density remains relatively constant compared to the CP//AC device.

4. Conclusions

This study demonstrates the successful engineering of an NCP@NCSe heterostructure electrode via a two-step process, providing hybrid charge-storage mechanisms and significantly improving the electrochemical performance of the supercapattery device. The NCP@NCSe||AC supercapattery device exhibits a superior charge-storage capacity of 251.7 mAh g^{-1} at a constant current density of 1 mA g^{-1}. More significantly, the assembled supercapattery delivers an energy density of 68.5 Wh kg^{-1} at a power density of 272.2 W kg^{-1} and exhibits exceptional stability, with 85.7% retention after 5000 cycles at 5 mA g^{-1}. The presence of a well-defined $NiCoSe_2$ hetero-interface resulted in a massive increase in the number of active redox sites by providing optimal ionic diffusion pathways and enabling the rapid electron transport. These structural-property enhancements had a positive impact on the device's energy and power densities, with the former increasing dramatically and the latter remaining relatively stable, thereby demonstrating the heterostructure architecture's underlying efficiency. The exhibited hetero-architecture represents a scalable, compositionally flexible platform that can be expanded to a wide variety of transition-metal phosphates and mixed-phase electrodes. This approach opens a very promising pathway for the development of next-generation electrochemical energy storage systems with high energy and power, and long life, for future energy-demanding applications such as flexible electronics and integrated power modules.

CRediT authorship contribution statement

N. Padmanathan: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **R. Sasikumar:** Writing – review & editing, Investigation. **Kafil M. Razeeb:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Authors' statement

All authors acknowledged responsibility for the full content of this manuscript, consented to its submission to the journal, examined all the results, and approved the final version.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.est.2026.122180.

Data availability

Data will be made available on request.

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