# Molybdenum-Doped Nickel Disulfide (NiS₂:Mo) Microspheres as an Active Anode Material for High-Performance Durable Lithium-Ion Batteries

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**ABSTRACT:** Transition-metal sulfides (TMSs) are promising anode materials for lithium-ion batteries (LIBs) as they exhibit anomalously high specific capacities. However, the electrodes made on TMSs possess low electronic conductivity and poor specific capacity retention, which hinder their application in LIBs. Herein, we report a one-step, simple, hydrothermal technique for synthesizing molybdenum-doped nickel disulfide (NiS₂:Mo) microspheres with varying Mo contents (0, 5, and 10 wt %) and their performance as anode materials in LIBs. Mo doping was found to improve the electronic conductivity, structural stability, and reduce charge transfer resistance between the electrode/electrolyte interface of NiS₂ microspheres, thereby achieving a superior electrochemical performance in LIBs. The anode made of NiS₂:Mo microspheres with 5 wt % Mo registered a maximum specific capacity and cycling durability. It delivered an outstanding initial specific capacity of 1605 mAh g$^{-1}$ at 0.1 Ag$^{-1}$ and exhibited exceptional cycling stability with a reversible discharge capacity retention of 713.3 mAh g$^{-1}$ after 120 cycles and Coulombic efficiency of 98.42%. Such exceptionally high specific capacity and high charge−discharge capacity retention of the NiS₂:Mo (5%) microspheres indicate that the material is a promising anode material for LIBs and other advanced energy storage applications.

**KEYWORDS:** nickel disulfide, molybdenum doping, green fabrication, Piper-longum fruit extract, anode materials, lithium-ion battery
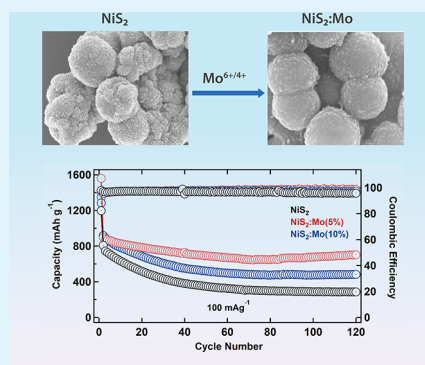
## 1. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have drawn much attention in recent times as one of the most attractive class of energy storage devices, capable of meeting future energy demands in a sustainable way.[1,2] Since the first rechargeable LIBs were commercially developed by Sony Corporation, Japan, in 1991, using LiCoO₂/C as an active electrode material,[3] LIBs become ubiquitous in everyday life because of their versatile applications, including in electronic devices, electric vehicles, energy storage grids, etc.[4−6] However, the utilization of LIBs on a large scale has been significantly hindered because of the low energy density of anode materials.[7] Although graphite-based materials have been employed widely for LIB anodes, they often exhibit a relatively low specific capacity. In fact, the theoretical specific capacity of graphite is only 372 mAh g$^{-1}$. Thus, its practical utilization in LIBs has fallen short of expectation.[8] To improve the energy storage capacity and cycling durability of LIBs, a tremendous research effort has been devoted recently for developing efficient and stable anode materials.[9−11] Specifically, anode materials based on transition-metal oxide (TMO) nanostructures[12,13] and their carbonaceous hybrid composites[14] have attracted much attention, since they can deliver outstanding

specific capacities in 700−1200 mAh g$^{-1}$ range, which are about 3-fold higher than the specific capacities of commercial graphitic carbon-based anodes.[13] However, these electrodes still suffer from the large volume expansion during charge−discharge cycling, affecting the cycling stability of the LIBs.[15] Hence, the development of anode materials that are capable of delivering high charge capacity and high cycling stability is of immense importance for meeting the growing demand of high-capacity anodes for LIBs.

Recently, nanostructured transition-metal sulfides (TMSs) have gained increasing attention due to their remarkable lithium storage performance, exceptionally high specific capacity and prolonged cycling stability both in LIBs and sodium-ion batteries (SIBs).[16−18] For instance, TMS nanostructures such as ZnS,[19] Cu₂S,[20] NiS₂,[21] CoS₂,[22] MoS₂,[23] and FeS₂,[24] have been utilized as high-capacity anodes in LIBs/
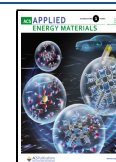
SIBs due to their excellent lithium storage performance and unique electronic structures.[25] In particular, nickel disulfide ($NiS_2$) is seen to be chemically stable among the other nickel sulfide phases like $NiS_2$, $Ni_3S_2$, $Ni_3S_4$, and $Ni_7S_6$ with a considerably high theoretical specific capacity (807 mAh $g^{-1}$).[21] Unfortunately, $NiS_2$ also exhibits low electronic conductivity and lacks structural stability, thus inevitably undergoes volume expansion and structure failure during longer charge−discharge cycling during the lithium insertion/exertion process, resulting in poor cycling stability and severe pulverization.[18] One successful approach to tackle these issues of anode materials is the doping TMOs/TMSs with metal ions. Several mono- and multivalent dopant ions, such as $Cu^{2+}$, $Co^{2+}$, $Mo^{6+}$, $Nb^{5+}$, $Cr^{3+}$, $Ti^{4+}$, etc., were used to dope TMOs/TMSs and tested as anode materials for LIBs.[24,26−28] Among the tested dopants, Mo was seen to improve the specific capacity and cycling stability of TMO/TMS electrodes remarkably.[29,30] For instance, Chen et al.[30] showed that doping of porous $WO_2$ with Mo stabilizes its structure and improves its electronic conductivity, resulting in its performance enhancement as the electrode material in LIBs. Recently, we have shown that Mo doping in $Cu_2O$-based anodes can substantially enhance its specific capacity (up to 1128 mAh $g^{-1}$ at 0.1 A$g^{-1}$) and cycling stability in LIBs.[31] Considering the impressive performance in previous studies, we considered Mo doping in $NiS_2$ microspheres to utilize them as the anode material for LIBs. As the average Shannon radii[32] of $Mo^{6+}$ (0.59 Å)[31] and $Ni^{2+}$ (0.69 Å) ions are relatively close, the replacement of $Ni^{2+}$ by $Mo^{6+}$ in the $NiS_2$ lattice is highly feasible. Previous studies have revealed that $Mo^{6+}$ ions can substitute the $Ni^{2+}$ ions from the $NiS_2$ lattice effectively at relatively low Mo concentrations (<1 mol %). Above this concentration, only a fraction of $Mo^{6+}$ ions occupies the $Ni^{2+}$ sites, segregating the remaining fraction toward the surface of $NiS_2$.[33] Moreover, Mo doping can reduce the irreversible capacity loss due to lower side reactions of the electrode with electrolytes and promote the fast ionic transport at the surface of anode materials.[34]

To enhance the electrochemical performance of these anodes further, the TMSs and TMOs with micro-/nanosphere morphologies composed of small nanosized particles or multishell structures have been synthesized and utilized as anode materials for LIBs with good performances.[19,35,36] These microstructures could provide a large number of surface sites for lithium storage, promote the transport of $Li^+$ and $e^−$, and also buffer the volume change during repeated cycling.[37] Over the past few years, numerous synthetic approaches such as wet-chemical synthesis,[38] template-assisted synthesis,[39] and hydrothermal and solvothermal processes have been explored for fabricating TMS/TMO microspheres.[19] Among the explored methods, green-solvent-assisted hydro-/solvothermal processes have been recognized as attractive and efficient synthesis platforms for fabricating uniform-sized TMS/TMO microstructures.[40] Recently, green and environmentally friendly solvents such as deep eutectic solvents (DESs)[41] and various plant/fruit extracts[31] have been utilized for the hydro-/solvothermal synthesis of TMO and TMS microstructures in a controlled manner. Specifically, the Piper-longum extract obtained from long Piper-longum fruits has been utilized as a solvent and a stabilizing agent in the synthesis of metallic NPs[42,43] and metal oxide nanostructures.[31,42] The extract obtained from the long Piper-longum fruits has been traditionally known as a medicine for treating a variety of diseases including cancer.[42] Previous studies have revealed that Piper-

longum fruit extract contains piperine, piperlongumine, sylvatin, pipermonaline, and several phytochemicals containing phenol and/or polyol groups.[43] The presence of such groups in the extract plays a key role and makes the extract an effective stabilizing and reducing agent for various metal ions.[43,44]

In this article, we present a one-step hydrothermal process for the synthesis of porous $NiS_2$ and Mo-doped $NiS_2$ microspheres using the Piper-longum fruit extract as a solvent. $NiS_2$:Mo microspheres with different Mo contents were prepared and utilized as anode materials for LIBs. The anode fabricated with $NiS_2$:Mo (5%) microspheres manifested the best electrochemical performance with a specific capacity as high as 1605 mAh $g^{-1}$ at 0.1 A $g^{-1}$, high rate capability, and excellent cycling stability. The superior performance of the porous $NiS_2$:Mo (5%) microspheres has been associated with their improved structural stability, electrical conductivity, and a fast ion diffusion between the anode and the electrolyte solution.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999%), thiourea ($NH_2CSNH_2$, 99.0%), ammonium molybdate tetrahydrate, ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), and ethyl alcohol (anhydrous, ≥99.5%) were purchased from Sigma-Aldrich, Korea. All of the chemicals were of analytic grade and utilized as received without further purification. Deionized water ($\rho > 18.2$ Ω-cm) was used for all synthesis and electrochemical experiments.

**2.2. Preparation of Piper-longum Fruit Extract.** Ripped Piper-longum fruits were collected from Piper-longum (long pepper) plants grown in the southern part of India. The collected Piper-longum fruits were first washed with DI water several times to remove surface attached contaminations such as dust and then allowed to dry under shade to eliminate the moisture. After drying, the fruits were ground well in a commercial electric mixture grinder, obtaining a fine powder, which was utilized to prepare the Piper-longum fruit extract. About 0.5 g of the prepared powder was dispersed in 50 mL of ethanol under magnetic stirring for 30 min. Finally, the solution mixture was filtered using a Whatman filter paper to have a homogeneous Piper-longum fruit extract, which was stored at ambient temperature and utilized for the synthesis of $NiS_2$ and $NiS_2$:Mo microspheres.

**2.3. Synthesis of $NiS_2$ and $NiS_2$:Mo microspheres.** $NiS_2$ and $NiS_2$:Mo microspheres were prepared by a single-step, Piper-longum extract-assisted hydrothermal process, where the fruit extract was used as an effective solvent. In a typical synthesis process of the $NiS_2$ microsphere, 5 mL (50 m mol) of nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and 5 mL (50 mM in DI water) of thiourea ($NH_2CSNH_2$) were mixed with 50 mL of Piper-longum fruit extract under magnetic stirring at room temperature. After 1 h of magnetic stirring, the reaction mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave. The capped autoclave containing the reaction mixture was then heated to 200 °C (at 5 °C/min heating rate) and kept at this temperature for 12 h. After that, the autoclave was cooled to ambient temperature. The obtained product was separated by centrifugation, washed four times with water and ethanol, and dried at 60 °C for 6 hours. The Mo-doped $NiS_2$ ($NiS_2$:Mo) samples with varied Mo contents (0.0, 5.0, and 10.0 wt %) were prepared using a similar protocol, and only the reaction mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $NH_2CSNH_2$ was allowed to magnetic stirring for 2 h in the Piper-longum extract solvent. Then, different amounts of a molybdenum precursor ($(NH_4)6Mo_7O_{24} \cdot 4H_2O$) were added to the reaction mixture before its hydrothermal treatment.

**2.4. Characterization of Doped and Undoped Microspheres.** *2.4.1. Morphology and Structural Characterization.* Crystallinity and the crystal structure of the as-grown microsphere samples were examined by X-ray diffraction (XRD, X'Pert PRO PANalytical) utilizing a Cu Kα X-ray radiation source ($\lambda = 0.15406$ nm). A field emission-scanning electron microscope (FE-SEM, Hitachi SU800) coupled with an energy-dispersive X-ray spectrom-

Scheme 1. Schematic Presentation of the Steps Involved in the *Piper-longum* Fruit Extract-Assisted Hydrothermal Process Utilized for the Synthesis of NiS$_2$:Mo Microspheres
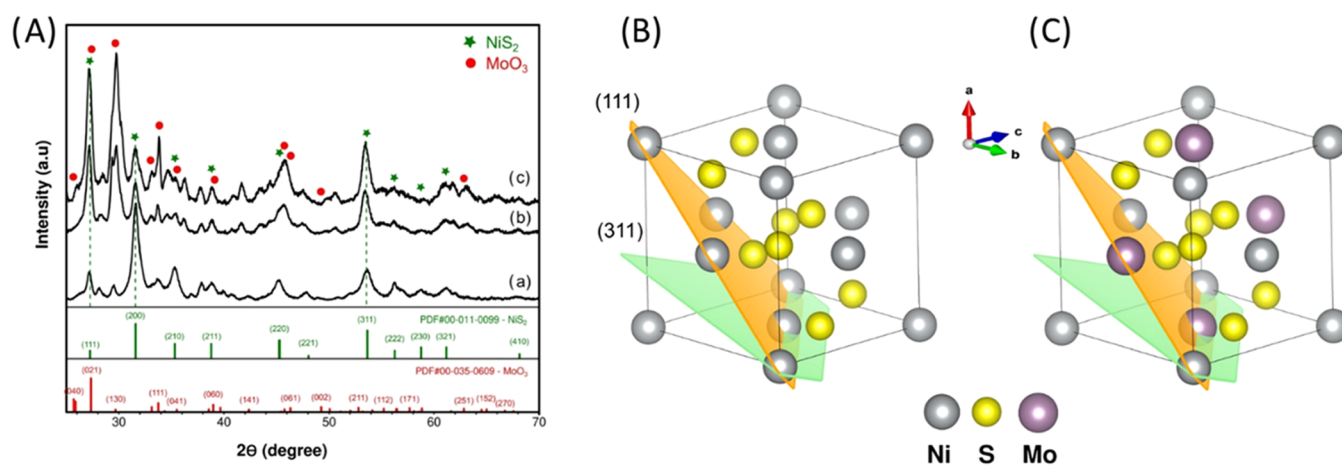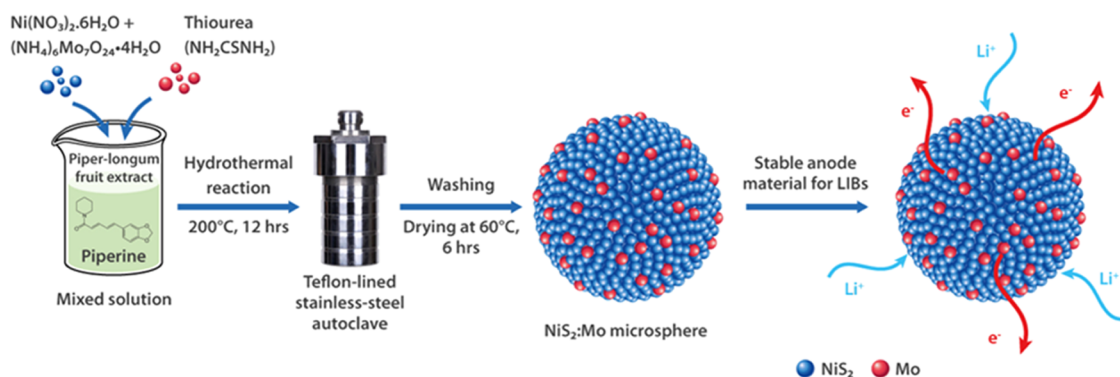


Figure 1. (A) Typical XRD patterns of (a) NiS$_2$, (b) NiS$_2$:Mo (5%), and (c) NiS$_2$:Mo (10%) microspheres. The red and green vertical lines correspond to the peak positions of standard NiS$_2$ and MoO$_3$, respectively. (B) Structure of pure NiS$_2$ and (C) possible Mo dopant sites in NiS$_2$ lattice.

eter (EDX) operated at 15 kV was utilized to analyze the morphology, surface structure, and composition of the synthesized microspheres. A JEOL JE2300T transmission electron microscope (TEM) operating at 120 kV was utilized to record the TEM and HR-TEM images for a detailed analysis of the surface morphology and fine structure of the samples. X-ray photoelectron spectroscopy (XPS) was utilized to analyze the composition of the samples and the oxidation states of their constituting elements. An Omicron (Nanotechnology, Germany) spectrometer operating at ultrahigh vacuum ($1 \times 10^{-10}$ Torr) and a Al K$_\alpha$ radiation source (1486.6 eV) was utilized for this purpose.

*2.4.2. Electrochemical Characterization.* For the fabrication of LIB anodes, first, a homogeneous paste was prepared by mixing the active material (as-synthesized sample), 10 wt % polyacrylic acid-carboxymethyl cellulose binder, and 15 wt % acetylene black (AB) in DI water. The viscous slurry was then cast over a clean commercial copper foil (Sigma-Aldrich, 99.0%) by doctor blading and allowed to dry in a vacuum oven at 120 °C for 12 h. The deposited film was then pressed to accomplish an intimate contact between the active material and the copper current collector. The area of the anode was about 1.539 cm$^2$, and the estimated average loading (active material) was about 1.5 mg cm$^{-2}$. Lithium metal foils were used both as the reference and the counter electrode, while a thin polypropylene membrane was employed as a separator. For half-cell fabrication, a mixture of 1M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio was employed as an electrolyte. All of the electrochemical measurements were carried out by assembling 2032 standard battery coin cells inside an argon-filled glovebox. An electrochemical impedance spectrometer (EIS, Zive MP2, Seoul, South Koria) in a multichannel electrochemical workstation was employed to record the EIS spectra and CV profiles.

## 3. RESULTS AND DISCUSSION

As shown in Scheme 1, pure NiS$_2$ and Mo-doped NiS$_2$ microspheres of uniform sizes were synthesized through a single-step hydrothermal process in the presence of thiourea and the *Piper-longum* fruit extract. Previous studies revealed that the S atoms of the thiourea molecules have a strong binding affinity with different metal cations, such as Zn$^{2+}$, Ni$^{2+}$, etc.[19,45] In the present case, during the hydrothermal reaction, Ni$^{2+}$ ions from the Ni(NO$_3$)$_2$·6H$_2$O precursor react with S$^{2-}$ ions generated from the decomposition of thiourea (NH$_2$CSNH$_2$). As a result, the Ni$^{2+}$ ions are reduced and form NiS$_2$ nanoparticles. In the case of Mo-doped NiS$_2$, the S$^{2-}$ ions from thiourea react with the Ni$^{2+}$ and Mo$^{4+/6+}$ ions during the hydrothermal treatment to form Mo-doped NiS$_2$ NPs. The long-chain piperine present in the *Piper-longum* fruit extract contains phenolic groups, which serve as a surfactant for the controlled growth of NiS$_2$ or NiS$_2$:Mo nanoparticles.[31] The slow reduction of metal ions by thiourea under the hydrothermal reaction conditions in the presence of *Piper-longum* extract leads to a controlled aggregation of small particles, producing porous spherical microstructures. For a better understanding of the role of *Piper-longum* fruit extract in the formation of microsphere structures, controlled synthesis of bare NiS$_2$ and NiS$_2$:Mo (5%) samples was carried out by replacing the *Piper-longum* fruit extract with ethanol as a solvent keeping all other synthesis conditions the same. Figure

S1 (Supporting Information) shows the SEM images of the bare $NiS_2$ and $NiS_2$:Mo (5%) samples obtained without *Piper-longum* fruit extract in the reaction mixture. As can be seen, the final products were not well-defined microsphere structures, instead, microstructures of flower-like morphology were formed. This clearly indicates that the *Piper-longum* fruit extract plays a key role in the formation of microsphere morphologies.

Powder X-ray diffraction (XRD) analysis was performed to analyze the crystalline structure and phase of the as-prepared microsphere samples. Figure 1A shows the XRD patterns of the pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) samples. As can be noticed in Figure 1A, the pure $NiS_2$ samples revealed several well-defined diffraction peaks, and the position of all of the peaks match well with the standard peak positions of cubic $NiS_2$ in pyrite phase (JCPDS No. 00-011-0099).[21] Appearance of intense and well-defined diffraction peaks indicates the good crystallinity of the as-prepared $NiS_2$ sample. XRD spectra of the $NiS_2$:Mo samples revealed additional peaks, which could be readily indexed to the $MoO_3$ phase (JCPDS No. 00-005-0600).[46] It is important to mention that no obvious peaks corresponding to the other phase such as $MoS_2$ were found. Notably, the intensity of the diffraction peaks associated with the (111) and (311) planes of $NiS_2$ increased with the increase of Mo content, indicating the incorporation of $Mo^{4+/6+}$ ions through $Ni^{2+}$ substitution in the $NiS_2$ lattice. Considering that the ionic radii of $Mo^{4+}$(0.65 Å) and $Mo^{6+}$ (0.59 Å) ions are relatively close to the ionic radius of $Ni^{2+}$ (0.69 Å) ions, it is reasonable to consider that $Mo^{4+/6+}$ ions occupy $Ni^{2+}$ sites in the $NiS_2$ lattice. However, doping a higher Mo concentration could increase the amount of $Ni^{2+}$ ions at the expense of $Ni^{3+}$ ions.[33] Average crystallite sizes estimated from the full width at half-maximum values of the XRD peaks were about 18.0, 21.6, and 17.1 nm for the pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) samples, respectively. Based on the XRD results, the Mo site occupancy in the unit cell of $NiS_2$ is proposed. $NiS_2$ bears a cubic crystal structure with the space group $Pa3$ (205), in which the Ni atoms occupy the sites in the fcc sublattice (Figure 1B).[47] The doped Mo atoms incorporate into the $NiS_2$ lattice, possibly by replacing the $Ni^{2+}$ ions in the {111} and {311} lattice planes as displayed in Figure 1C.

The morphological characteristics of the as-obtained pure $NiS_2$ and Mo-doped $NiS_2$ microspheres were explored using field emission-scanning electron microscopy (FE-SEM). Figure 2 shows the low- and high-magnification SEM images of $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) samples. The formation of uniform microspheres of about 500 nm diameter in the pure $NiS_2$ sample can be clearly seen in the low-magnification SEM image presented in Figure 2a. A high-magnification SEM image (Figure 2b) of the sample revealed that the $NiS_2$ microspheres are composed of tiny particles assembled together, which act as the building blocks of the microspheres. Due to the same reason, the microspheres have rough surfaces.

In the case of the $NiS_2$:Mo (5%) sample (Figure 2c,d), although the original spherical morphology was preserved, the surface roughness of the microspheres increased, which was due to the partial substitution of $Ni^{2+}$ by $Mo^{6+}$ atoms and the segregation of the remaining Mo atoms toward the surface of $NiS_2$. With the increase of Mo concentration from 5 to 10 wt %, the roughness of the $NiS_2$ microsphere surface increased (Figure 2e,f). This could be mainly because of the high Mo content in the reaction mixture, as a major fraction of the Mo atoms segregates to the $NiS_2$ surface. Moreover, with higher
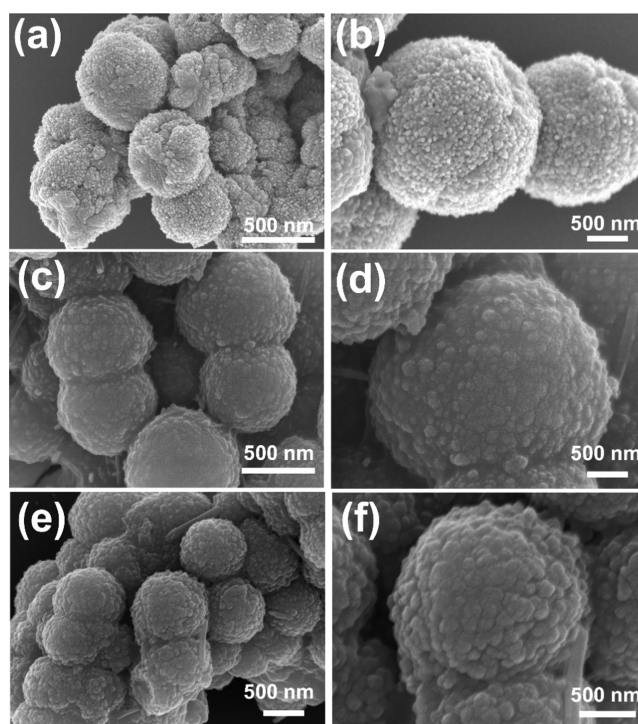


**Figure 2.** Typical SEM images of (a, b) pure $NiS_2$, (c, d) $NiS_2$:Mo (5%), and (e, f) $NiS_2$:Mo (10%) microsphere samples. The images in the left and right columns correspond to low- and high-magnification images, respectively.

Mo doping (about 10%), the particle size is found to be decreased (Figure 2e,f), which is consistent with the crystallite size estimated from XRD peaks. Such a decrease of particle size is due to the partial incorporation of Mo ions at the $Ni^{2+}$ sites and subsequent surface segregation of remaining Mo atoms, as has been observed by other research groups.[30,33]

To further explore the surface structure and morphology of the as-prepared $NiS_2$:Mo samples, they were analyzed in a transmission electron microscope (TEM). Figure 3a,b shows the typical TEM images of the $NiS_2$:Mo (5%) microsphere sample. The spherical shape and rough surface morphology of the microstructures are very clear in the TEM images. The TEM-estimated particle size of the microstructures is ~500 nm, which is in good agreement with the size estimated from their SEM analysis. Figure 3c shows the typical high-resolution TEM (HR-TEM) image of a $NiS_2$:Mo (5%) microsphere sample. The crystalline $MoO_3$ and $NiS_2$ regions in the microsphere can be clearly distinguished from the respective interplanar spacing in the magnified sections (marked by square boxes in Figure 3c) presented in Figure 3d,e, respectively. As can be seen, the estimated lattice spacing values are about 0.39 and 0.283 nm (Figure 3d,e), which are associated with the (110) plane of $MoO_3$[48] and (200) plane of $NiS_2$,[21] respectively. Ni, S, and Mo distributions in the microsphere were recorded by EDX mapping. As can be noticed in the EDX mapping images presented in Figure 3f, all three elements remained uniformly distributed in the microspheres. EDX spectra of the samples (Figure S2, Supporting Information) revealed the emissions of Ni, S for $NiS_2$, and Ni, S, Mo, and O elements for $NiS_2$:Mo microspheres. The estimated Mo content in the $NiS_2$:Mo (5%) and $NiS_2$:Mo (10%) samples was about 4.23 and 8.96 wt % (Table S1, Supporting Information), which are very close to the nominal
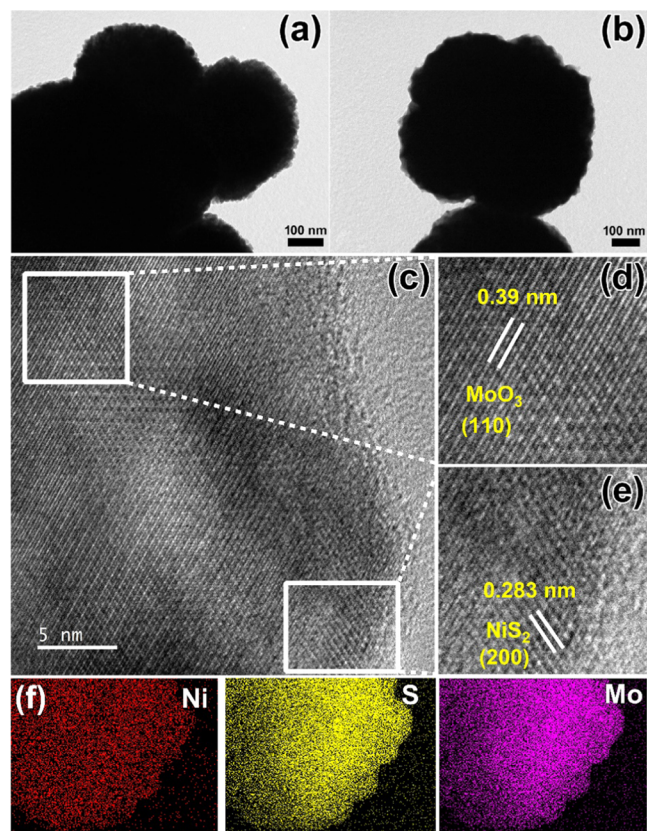
**Figure 3.** (a, b) Typical TEM images and (c−e) HR-TEM images of the NiS$_2$:Mo (5%) microspheres. (f) EDX elemental mapping images showing the uniform distribution of Ni, S, and Mo elements in the microspheres.
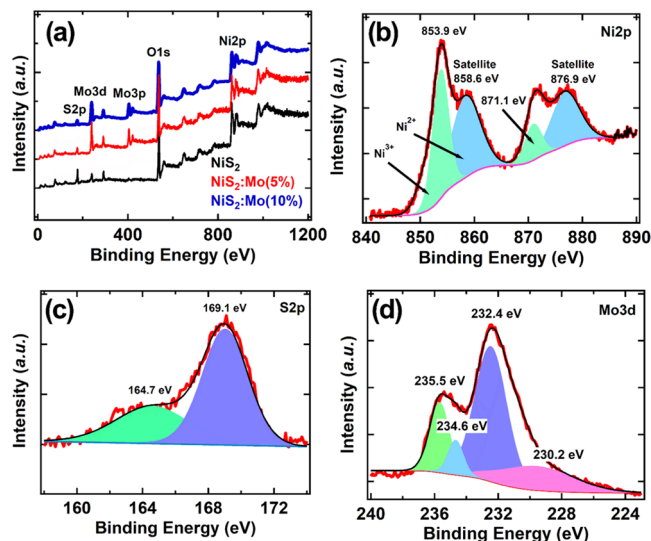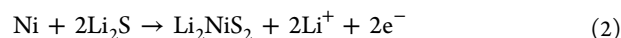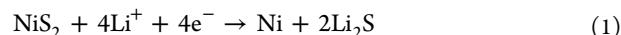


**Figure 4.** XPS (a) survey scans of the pure and Mo-doped NiS$_2$ microspheres. (b) Ni 2P, (c) S 2P, and (d) Mo 3d core-level spectra of the NiS$_2$:Mo (5%) microsphere sample, along with their deconvoluted components.

Mo contents in the corresponding reaction mixtures used for the hydrothermal reaction.

To identify the elemental composition and valence states of the constituting elements, the NiS$_2$ and NiS$_2$:Mo microsphere samples were analyzed by X-ray photoelectron spectroscopy (Figure 4). The survey XPS spectra of the samples presented in Figure 4a clearly show the appearance of emission peaks of Ni, S, Mo, and O elements in the NiS$_2$:Mo microsphere samples and the absence of Mo emission for the pure or undoped NiS$_2$ microsphere sample, confirming their purity. The core-level Ni 2P emission of the NiS$_2$:Mo (5%) sample (Figure 4b) revealed peaks at binding energies 871.1 and 853.9 eV, associated with the 2P$_{1/2}$ and Ni 2p$_{3/2}$ spin−orbit splitting of Ni$^{3+}$ species.[49−51] The two satellite peaks that appeared around 276.9 and 258.6 eV are associated with the Ni$^{2+}$ state of nickel.[51,52] The results confirm that Ni in the NiS$_2$:Mo (5%) sample remained in Ni$^{3+}$ and Ni$^{2+}$ oxidation states. Figure 4c shows the S 2P core-level emission of the NiS$_2$:Mo (5%) sample. The spectrum revealed two intense peaks centered at around 169.1 and 164.7 eV binding energies, which correspond to the 2P$_{1/2}$ and 2P$_{3/2}$ orbitals of divalent sulfide ions S$_2$$^{2−}$ in NiS$_2$.[26,52] Finally, the core-level Mo 3d emission of the sample (Figure 4d) reveals that the bands corresponding to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ orbitals of Mo$^{6+}$ peaked around 232.4 and 235.5 eV, respectively.[46,53] Also, two low-intensity peaks appeared around 230.2 and 234.6 eV, which correspond to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ orbitals of Mo$^{4+}$.[54] Although these results indicate that Mo remains in Mo$^{6+}$/Mo$^{4+}$ mixed oxidation states in the NiS$_2$:Mo (5%) sample from the areas of the

deconvoluted bands in Figure 4d, we can see that only a small fraction of Mo atoms in the sample remains in Mo$^{4+}$ oxidation state.

The lithium storing properties of the electrodes made of as-prepared NiS$_2$:Mo (5%) microspheres were first studied by cyclic voltammetry (CV). Figure 5a presents the typical CV curves of the electrode fabricated with NiS$_2$:Mo microspheres with 5 wt % Mo incorporation in the first three successive sweeping cycles over a potential range of 0.01 to 3.0 V (*vs* Li$^+$/ Li) at 0.1 mVs$^{−1}$ scan rate. In the first cathodic scan, two peaks appeared at around 1.86 and 0.742 V (*vs* Li$^+$/Li). While the peak appeared at 1.86 V is associated with Li$^+$ insertion and conversion of NiS$_2$ into metallic Ni,[50] the peak appeared at 0.742 V can be ascribed to the irreversible decomposition of the electrolyte solution, followed by an irreversible formation of a solid electrolyte interface (SEI) film over the surface of the electrode material.[55,56] Notably, after the first cycle, the height of the peak at 0.742 V significantly reduced, suggesting that the SEI film has been formed during the first cycle. In the following first anodic scan, an intense peak appeared at 0.992 V and two less intense peaks appeared around 1.35 and 2.05 V (*vs* Li$^+$/Li). The peak appeared at 0.992 V is related to the partial dissolution of the SEI film.[27] On the other hand, the peak appeared around 2.05 V is associated with the delithiation of Li$^+$ and oxidation of metallic Ni and formation of NiS$_2$,[57] and the peak appeared around 1.35 V corresponds to the oxidation of Mo to form MoO$_3$.[58] These conversion reactions can be described by the following equations[59]

$$NiS_2 + 4Li^+ + 4e^- \rightarrow Ni + 2Li_2S \tag{1}$$

$$Ni + 2Li_2S \rightarrow Li_2NiS_2 + 2Li^+ + 2e^- \tag{2}$$

It should be noted that the oxidation peak at 1.358 V disappeared in the 3$^{rd}$ cycle, while the other peaks remained unchanged, which indicates that the incorporation of Mo in NiS$_2$ reduces the conversion reaction reversibility slightly, as observed in previous studies.[58] After the first CV cycle, the observed reduction peaks during the first cycle appeared around 1.86 and 0.742 V were shifted to 1.87 and 0.73 V, and
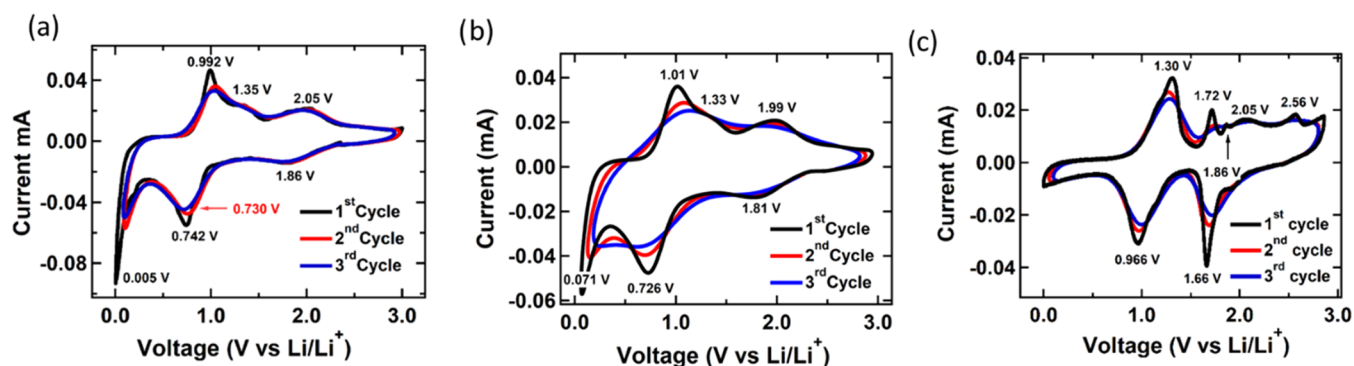
**Figure 5.** CV curves of (a) $NiS_2$:Mo (5%), (b) $NiS_2$:Mo (10%), and (c) bare $NiS_2$ microsphere electrodes in the 1st, 2nd, and 3rd sweeping cycles recorded in the 0.01−3.0 V (*vs* Li/Li$^+$) range at a scan rate of 0.1 mV s$^{-1}$.
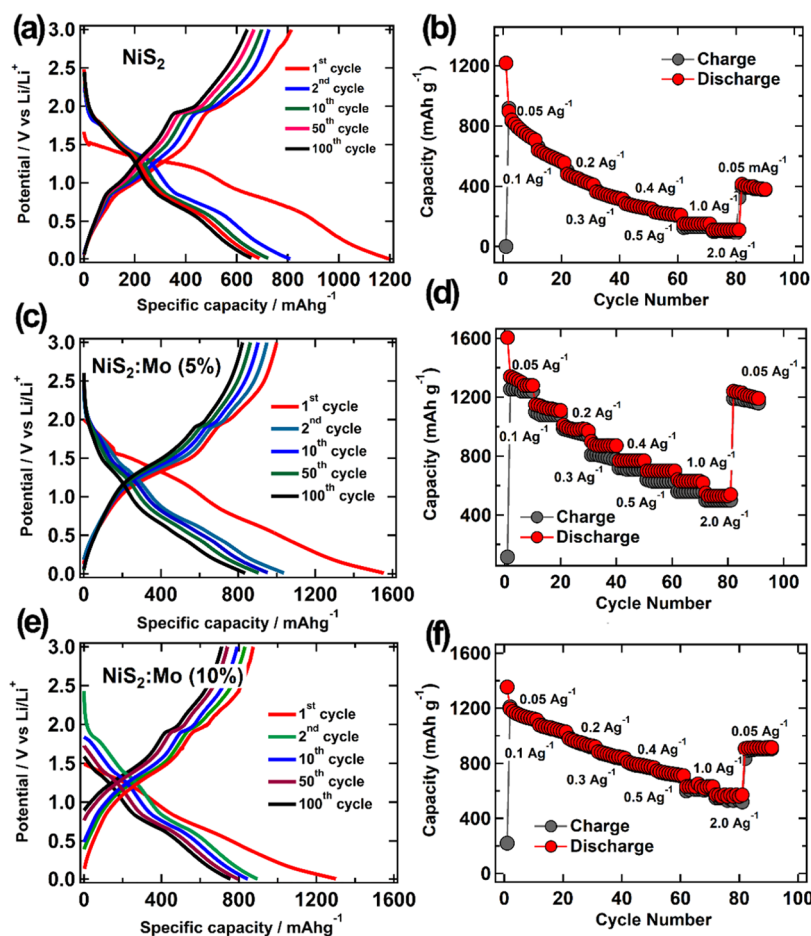


**Figure 6.** Typical galvanostatic charge−discharge curves of (a) pure $NiS_2$, (c) $NiS_2$:Mo (5%), and (e) $NiS_2$:Mo (10%) microspheres in the potential window 0.01−3.0 V (*vs* Li/Li$^+$) at a current density of 0.1 Ag$^{-1}$. (b, d, f) Rate capability of pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) microspheres at various current densities between 0.05 and 2.0 A g$^{-1}$.

the oxidation peaks at 0.992 and 2.05 V were shifted to 1.01 and 2.04 V, respectively. The shifts in the redox peaks during the later cycles could be ascribed to the improved diffusion kinetics of Li ions.[27] Notably, the redox peaks exhibit identical shape and position during the second and third cycles, which implies the excellent cycling stability of the $NiS_2$:Mo electrode.[60]

For a better comparison, the CV profiles of $NiS_2$:Mo (10%) and bare $NiS_2$ microsphere electrodes were recorded at a scan rate of 0.1 mVs$^{-1}$ (Figure 5b,c). The CV curve in the first cycle of the $NiS_2$:Mo (10%) electrode exhibited redox peaks similar

to that of the $NiS_2$:Mo (5%) electrode, with a slight variation in shape. The CV curve for the bare $NiS_2$ electrode acquired in the first cycle revealed two prominent cathodic peaks located at 1.66 and 0. 966 V, which are associated with the conversion of $NiS_2$ to metallic Ni and the formation of SEI films on the electrode surface, respectively. On the other hand, the first anodic scan of the bare $NiS_2$ electrode revealed oxidation peaks located at 1.30, 1.72. 2.05, and 2.56 V. The oxidation peak revealed at 1.30 V is attributed to the decomposition of SEI films, whereas the peaks that appeared at 1.72 and 2.05 V correspond to the formation of $Li_xNiS_2$ and conversion of Ni

into $NiS_2$, respectively.[21,62] Notably, the intensities of the redox peaks for both the $NiS_2$:Mo (10%) and bare $NiS_2$ electrodes become weaker in the following cycles, indicating the low stability of the $NiS_2$:Mo (10%) and pure $NiS_2$ microsphere electrodes.

The electrochemical activity of the $NiS_2$:Mo anode toward $Li^+$ ion storage performance was studied in 20320-type standard battery coin cells with lithium metal as counter electrodes. To investigate the intrinsic properties of the fabricated electrodes, electrochemical galvanostatic charge—discharge cycling was employed in the potential range 0.01—3.0 V ($vs$ Li/$Li^+$) at a current density of 0.1 A$g^{-1}$. Figure 6a,c,e shows the representative galvanostatic charge—discharge curves of the pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) electrodes during the 1st, 2nd, 10th, 50th, and 100th cycles. As can be seen, all of the electrodes exhibit a series of plateaus at 1.5 V and below 1 V during the first discharge cycle due to the change of conversion reactions, which is in good agreement with the CV curves presented in Figure 5. The galvanostatic charge—discharge curves presented in Figure 6c indicate that the galvanostatic discharge capacity of the $NiS_2$:Mo (5%) electrode in its first cycle is about 1554.3 mAg $g^{-1}$, which decreased to 1037.9, 952.83, 906.15, and 836.89 mAg $g^{-1}$ in the subsequent 2nd, 10th, 50th, and 100th cycles, respectively. However, the electrode fabricated with pure $NiS_2$ microspheres registered discharge capacities of 1197.3, 809.3, 723.1, 688.9, and 657.3 mAg $g^{-1}$, and the electrode fabricated with $NiS_2$:Mo (10%) microspheres displayed specific discharge capacities of 1296.6, 896, 845.3, 802.4, and 760.0 mAg $g^{-1}$ for the 1st, 2nd, 10th, 50th, and 100th cycles, respectively. The results clearly indicate the superior discharge capacity of the $NiS_2$:Mo (5%) microspheres in comparison with the pure $NiS_2$ and $NiS_2$:Mo (10%) microspheres. Moreover, the change in the discharge capacity for the $NiS_2$:Mo (5%) sample after the first cycle is very small, indicating that the conversion reaction in the electrode is irreversible. The observed low-capacity loss for the $NiS_2$:Mo (5%) sample after the 1st cycle can be understood by the fact that decomposition of electrolytes and subsequent formation of a thin SEI film occurred during the 1st cycle, as commonly occurs for the TMS-based anodes operating through conversion reactions.[61,62] From the galvanostatic charge—discharge curves presented in Figure 6e, we can see that the discharge capacity of the electrode made of $NiS_2$:Mo (10%) microspheres is considerably lower than the discharge capacity of the electrode prepared with $NiS_2$:Mo (5%), although it is higher than the discharge capacity if the pure $NiS_2$ microsphere electrode.

The rate capability performance is regarded to be a critical parameter for the anode materials in LIBs for their successful implementation in commercial applications. Hence, the rate performance of the anodes was further studied at different cycling rates from 0.05 to 2.0 A $g^{-1}$ and then reverting back to 0.05 A $g^{-1}$ (Figure 6b,d,f). As shown in Figure 6d, the $NiS_2$:Mo (5%) electrode exhibits remarkably high rate performance relative to the electrodes made of pure $NiS_2$ and $NiS_2$:Mo (10%) microspheres. Specifically, the $NiS_2$:Mo (5%) microspheres deliver an average discharge capacity of 1310.2, 1110.6, 970.9, 871.4, 770.5, 700.1, 620.1, and 540.4 mAh $g^{-1}$ on stepwise increase of current density from 0.05 A $g^{-1}$ to 0.1,0.2,0.3, 0.4, 0.5, 1.0, and 2.0 A $g^{-1}$, respectively. Operating even at a high current density of 2.0 A $g^{-1}$, the $NiS_2$:Mo (5%) electrode delivered a high discharge capacity of 540 mAh $g^{-1}$, maintaining a high specific capacity. Notably, the observed

specific capacity value at a high current density (2.0 A $g^{-1}$) was about 41.2% of its initial discharge capacity value obtained at a low current density of 0.05 A $g^{-1}$ and also 1.5-fold greater relative to the theoretical specific capacity of an anode made of graphite (372 mAh $g^{-1}$).[8] Importantly, after operating at different current densities, the $NiS_2$:Mo (5%) microsphere electrode retained a specific capacity as high as 1191.3 mAh $g^{-1}$ when the applied current density was reversed back to 0.05 A $g^{-1}$ (Figure 6d), indicating its high rate capability. In contrast, the $NiS_2$ microsphere electrode (anode) showed poor rate capability, and its specific discharge capacity significantly dropped to 110.5 mAh $g^{-1}$ at 2.0 A $g^{-1}$ (Figure 6b). The $NiS_2$ microsphere electrode registered discharge capacities of 897.6, 555.7, 409.2, 313.6, 252.6, 207.5, 150.6, and 110.5 mAh $g^{-1}$ at current densities of 0.05, 0.1,0.2,0.3, 0.4, 0.5, 1.0, and 2.0 A $g^{-1}$, respectively. Upon reversing back, the current density to 0.05 A$g^{-1}$, it could recover only 380.8 mAh $g^{-1}$, which is significantly lower than the recovered current density by the $NiS_2$:Mo (5%) microsphere electrode (1191.3 mA h$g^{-1}$). Interestingly, at higher Mo contents, i.e., the $NiS_2$ microspheres with 10 wt % Mo doping ($NiS_2$:Mo (10%)) revealed a lower rate capability in comparison with the $NiS_2$:Mo (5%) microspheres. As shown in Figure 6f, the $NiS_2$:Mo (10%) electrode recorded discharge capacities of 1122.4, 1028.3, 919.7, 837.3, 772.3, 711.5,630.6, and 570.2 mAh $g^{-1}$ at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, and 2.0 A $g^{-1}$ current densities, respectively. When reverted back the current density value to 0.05 A $g^{-1}$, the electrode recovered a specific capacity of 914.4 mAh $g^{-1}$, which is significantly lower than the recovered specific capacity of the $NiS_2$:Mo (5%) electrode (1191.3 mAh $g^{-1}$). The low-rate performance of the $NiS_2$:Mo (10%) electrode is probably attributed to the lower structural stability of the $NiS_2$ microspheres upon high Mo loading (i.e., above 5%).

The cycling stability of the fabricated anodes was also studied at a higher current density of 100 mAg $^{-1}$. Figure 7
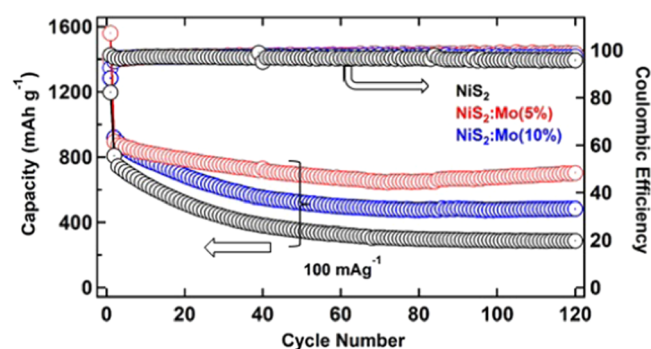


**Figure 7.** Comparison of long-term cycling stability and corresponding CEs of pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) at a charge density of 100 mA $g^{-1}$ for 120 cycles.

shows the comparison of cycling stability performance and Coulombic efficiencies (CEs) of the pure $NiS_2$, $NiS_2$:Mo (5%), and $NiS_2$:Mo (10%) microspheres. As can be seen in Figure 7, all three electrodes manifested a decrease of discharge capacity in the initial cycles (up to 50th cycle). Afterward, the specific capacity of the $NiS_2$:Mo microsphere electrodes increased slightly, without apparent capacity fading, until 120th cycle. However, the specific capacity of the bare $NiS_2$ electrode was found to decrease gradually. Such a trend might be due to the weak activation process in the $NiS_2$:Mo microsphere electrodes

in the initial 50 cycles and low $Li^+$ ions insertion due to Mo doping, which results in a slight decrease in the specific capacity gain. In addition, partial amorphization of $MoO_3$ during initial cycling could also lead to an increase in the $Li^+$ ion diffusion kinetics, providing more accessible active sites for $Li^+$ insertion, and hence causing a gradual increase of the specific capacity. Similar cycling-induced capacity gain has been previously observed for $MoO_3$-based anode materials.[30,47] Interestingly, the $NiS_2$:Mo (5%) microsphere electrode delivered an exceptionally high initial specific capacity of 900 mAh $g^{-1}$, which exceeded the theoretically predicted specific capacity value of $NiS_2$ (807 mAh $g^{-1}$),[21] as well as previously reported specific capacity values for the TMO/TMS-based anode materials, as shown in Table 1.[58,61,63−66] Even though

**Table 1. Comparison of the Performance of the $NiS_2$:Mo (5%) Microsphere Electrode with the Performance of Previously Reported TMS and Mo-Based Oxide Nanostructures in LIBs**

| nanostructured anode materials | current density (mA) | cycle numbers | reversible capacity (mAh $g^{-1}$) | reference |
|---|---|---|---|---|
| $ZnS_2$/CNT nanocomposite | 100 | 200 | 730 | 19 |
| $NiCo_2S_4$/N-doped carbon | 100 | 100 | 480 | 63 |
| $NiS_2$/$CoS_2$ NCs encapsulated N-doped carbon | 100 | 100 | 680 | 64 |
| $NiS_2$/FeS | 10 | 100 | 580 | 65 |
| $NiS_2$/$FeS_2$/N-doped carbon nanorods | 100 | 100 | 718 | 59 |
| NiO nanosheets arrays/NiS@$Ni_3S_2$ | 100 | 70 | 498.5 | 61 |
| $MoO_3$NPs/Graphite | 0.2 C | 120 | 712 | 66 |
| Ti-doped $MoO_3$ | 200 | 250 | 681.2 | 58 |
| $NiS_2$:Mo microspheres | 100 | 120 | 713.3 | this work |

the specific capacity of the electrode decreased gradually up to $50^{th}$ cycle, it retained a high reversible capacity of 713.3 mAh $g^{-1}$ even after 120 cycles, with CE as high as 98.43%.

On the other hand, the electrode made of pure $NiS_2$ microspheres showed a low reversible capacity, and the electrode made of $NiS_2$:Mo (10%) microspheres suffered an intermediate reversible capacity after 120 cycles. Specifically, the pure $NiO_2$ and $NiS_2$:Mo (10%) microsphere electrodes yielded reversible discharge capacities of 286.7 mAh $g^{-1}$ (95.84% CE) and 603.5 mAh $g^{-1}$ (97.23% CE) after 120 cycles, respectively. Nevertheless, these values are relatively lower in comparison with the discharge capacity of the $NiS_2$:Mo (5%) microsphere electrode (713.3 mAh $g^{-1}$), confirming its superior cycling stability performance. The decrease in rate performance and cycling stability of the $NiS_2$:Mo (10%) microsphere electrode could be attributed to the excess Mo doping, which leads to the reduction of reversibility of the conversion reaction, as observed in the CV curves presented in Figure 5b. Furthermore, a higher concentration of Mo in the $NiS_2$ lattice and only partial $Mo^{6+}$ ions occupy the $Ni^{2+}$ lattice; consequently, a high concentration of $Mo^{6+}$ ions segregates onto the surface of $NiS_2$ as observed in SEM results in Figure 2e,f. Such high $Mo^{6+}$ segregation toward the $NiS_2$ surface may significantly affect the electrode/electrolyte interface and $Li^+$ ion insertion/exertion

process, lowering the overall cycling stability performance of the $NiS_2$:Mo (10%) electrode.

To understand the electrochemical kinetics of Li ions in the $NiS_2$:Mo (5%) anode further, its CV curve was recorded with different scan rates in a Li half-cell. Figure 8a presents the CV profiles of the $NiS_2$:Mo (5%) electrode at different scan rates of 0.1, 0.2, 0.3, 0.4, 0.8, and 1.0 mV $s^{-1}$. The CV curves acquired at different scan rates have similar shapes. However, the peak current increased with the increase of the scan rate from 0.1 to 1 $mVs^{-1}$. In general, the total amount of charges stored in the anode material could be contributed by two different effects: (i) The pseudocapacitive effect originated from the electric double layer formation at the electrode−electrolyte interfaces and (ii) the diffusion-controlled insertion process in the faradaic reactions of the redox species. The contribution of these two effects can be evaluated by analyzing the CV response of an electrode at different scan rates, following the power-law relationship[67]

$$i = av^b \qquad (3)$$

where $a$ and $b$ are two adjustable parameters, $i$ is the current, and v is the sweep rate. The $b$ value can be obtained from the slopes of log (v) *vs* log (i) plots, as displayed in Figure 8b. The value of b suggests whether the reaction is limited by the diffusion-controlled process (when $b = 0.5$) or capacitive effect (when $b = 1.0$). From the log (i) *vs* log (v) plots in Figure 8b, the estimated b values for the anodic and cathodic peaks were about 0.95, 0.78, 0.84, 0.92, and 0.86 for peaks 1, 2, 3, 4, and 5, respectively. The b values estimated for the anodic and cathodic peaks suggest that the charge storage in the $NiS_2$:Mo (5%) electrode is mainly contributed by the pseudocapacitive process. In fact, similar current response behaviors have been seen for many metal sulfide-based anode materials.[19,20,68]

To estimate the capacitive contribution in the total stored charges for $NiS_2$:Mo (5%) quantitively, the obtained current can be described by the following equation[69]

$$i(V) = k_1 v + k_2 v^{1/2} \qquad (4)$$

where $k_1$ and $k_2$ are constants at a certain potential, $k_1 v$ and $k_2 v^{1/2}$ are associated with the surface-induced capacitive effect and diffusion-controlled insertion process, respectively. The pseudocapacitive contributions can be separated from the whole area of the CV curve by estimating the ratio of the integral area of pseudocapacitive currents (red color) as shown in Figure 8c. As can be seen in Figure 8c, the estimated pseudocapacitive contribution for $NiS_2$:Mo (5%) at a scan rate of 0.1 mV $s^{-1}$ covers the major portion of the CV curve (red-colored shaded area). Figure 8d shows the bar chart diagram, summarizing the ratio between diffusion-controlled contribution and pseudocapacitive process at varied scan rates. The estimated pseudocapacitive contributions were about 60.2, 66.1, 69.8, 73.1, 81.0, and 84.7% at the scan rates of 0.1, 0.2, 0.3, 0.4, 0.8, and 1.0 mV $s^{-1}$, respectively. As can be noticed, the percentage of pseudocapacitive contribution increases from 60.2 to 84.7% with an increase in scan rate from 0.1 to 1.0 mV $s^{-1}$. The results confirm that the high charge storage and enhanced rate performance of the $NiS_2$:Mo (5%) microsphere electrode are attributed to its pseudocapacitive charge storage behavior, which leads to a fast $Li^+$ ion insertion/extraction and enhancement of cycling life of the electrode.

To identify if there occurred any structural change in the $NiS_2$:Mo (5%) electrode upon performing cycling stability tests, the morphology of the electrode was examined by the
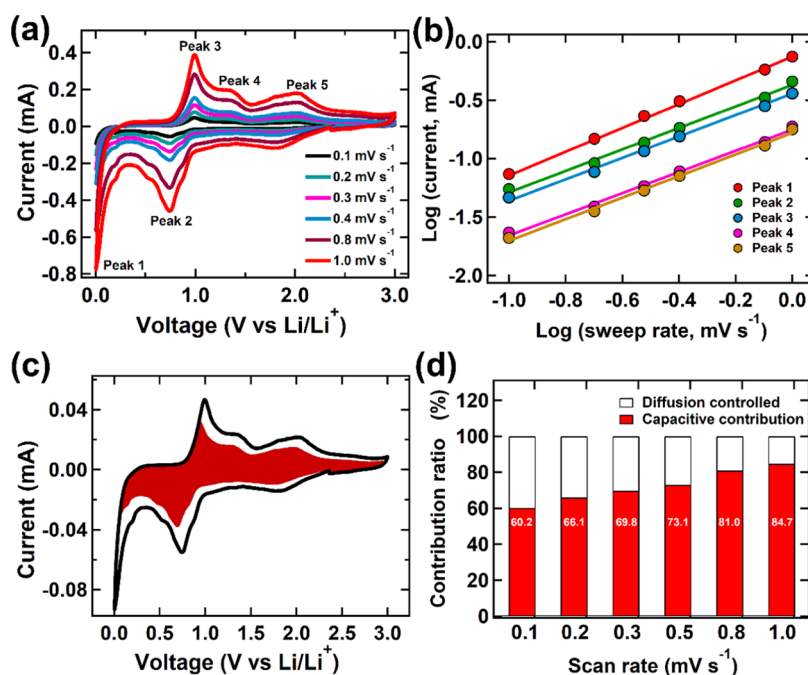
**Figure 8.** (a) CV curves of NiS$_2$:Mo (5%) microsphere electrodes at various scan rates from 0.1 to 1.0 mVs$^{-1}$; (b) log (I) *vs* log (V) plots for the electrode at each redox peak; (c) CV curves showing the separation of pseudocapacitive currents (red region) from the total current at a scan rate of 1 mVs$^{-1}$; (d) bar chart diagram showing the pseudocapacitive contribution at different scan rates ranging from 0.1 to 1 mVs$^{-1}$.

SEM and TEM (Figures S3 and S4, Supporting Information). The SEM images of the utilized (in 120 charge−discharge cycles) electrode revealed a very similar morphology as that of the unused electrode, indicating no significant damage occurred in the electrode or the material due to charge−discharge cycling (Figure S3). Furthermore, the TEM images obtained after the cycling tests (120 charge−discharge cycles) confirm that the NiS$_2$:Mo (5%) microspheres maintain their original morphology, and no cracks or aggregation occurred (Figure S4, Supporting Information). All of these results provide enough evidence of the structural stability of NiS$_2$:Mo microspheres, which is an essential requirement to overcome the challenges associated with the volume expansion of the anode material during charge−discharge cycling, and assure the long cycling stability of the fabricated anode.

Charge transfer resistance at the electrode/electrolyte solution interface was probed by recording the electrochemical impedance spectroscopy (EIS) spectra of the anodes. Figure 9 presents the Nyquist plots for the NiS$_2$, NiS$_2$:Mo (5%), and NiS$_2$:Mo (10%) microsphere electrodes. The inset (lower) of Figure 9 depicts the Randles equivalent circuit model utilized to fit the EIS spectra, which consists of charge transfer resistance ($R_{ct}$), solution resistance ($R_s$), constant phase element (CPE), and Warburg impedance ($Z_w$). As it is evident from the inset (upper) of Figure 9, the Nyquist plots for all three samples exhibited a high-frequency semicircle, followed by a quasi-linear variation in the low-frequency side. The $R_{ct}$ at the electrode/electrolyte interface can be obtained directly from the semicircle, while the quasi-linear part represents the solid-state diffusion resistance of Li$^+$ in the electrodes.[31,70] It is evident from Figure 9 that the NiS$_2$:Mo (5%) microsphere sample presents a semicircle of the smallest diameter, indicating its smallest $R_{ct}$ among the three electrodes. The $R_{ct}$ values estimated for the NiS$_2$, NiS$_2$:Mo (5%), and NiS$_2$:Mo (10%) microsphere electrodes were 17.28, 15.61, and 16.79 Ω, respectively. The EIS results indicated that the NiS$_2$:Mo (5%)
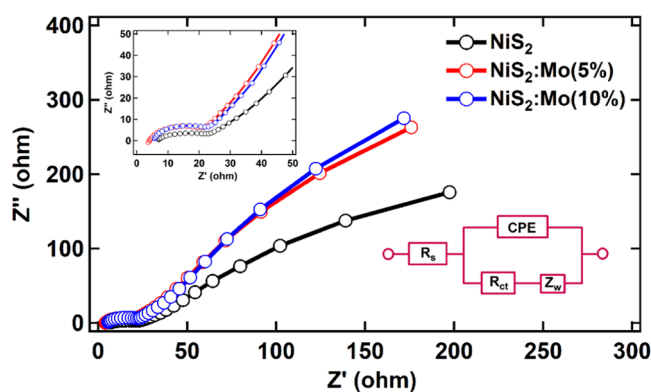


**Figure 9.** Nyquist plots for the pure NiS$_2$, NiS$_2$:Mo (5%), and NiS$_2$:Mo (10%) microsphere electrodes. Insets show the proposed equivalent circuit (lower) and magnified view of the high-frequency region (upper).

microsphere electrode had higher electrical conductivity than the pristine NiS$_2$ and NiS$_2$:Mo (10%) microsphere electrodes.

Based on the above experimental results, the improved electrochemical lithium storage performance of the NiS$_2$:Mo (5%) microsphere anode could be ascribed to several factors. First, incorporating Mo in low concentration (i.e., 5 wt %) significantly improves the electronic conductivity (Figure 9) and structural stability of NiS$_2$, which facilitate the ion and mass transfer between the electrolyte and the electrode interface. As a result, the anode made of NiS$_2$:Mo (5%) exhibits a long cycling life. Second, the unique microsphere morphology of the as-prepared NiS$_2$:Mo microspheres could provide an enhanced specific surface area and promote fast Li$^+$ ion insertion/exertion kinetics. Thus, the results obtained in this study clearly demonstrate that the anodes fabricated with NiS$_2$:Mo (5%) microspheres exhibit superior electrochemical performance toward lithium storage. The green synthesis

protocol implemented in the preparation of NiS₂:Mo microspheres can be easily implemented to fabricate other metal sulfide and metal oxide microstructures with enhanced electrochemical properties.

## 4. CONCLUSIONS

In summary, an environmentally friendly, hydrothermal synthesis strategy was designed to prepare porous NiS₂:Mo microspheres with varied Mo contents to utilize them as anode materials in LIBs. We demonstrate that Mo doping improves the electronic conductivity, charge transfer efficiency, and structural stability of the NiS₂ microspheres. The utilization of NiS₂:Mo microspheres in LIB anodes renders exceptional lithium storage capacity, high reversible specific capacity, along with prolonged cycling stability and good rate capability performance. In particular, Mo doping in moderate concentration (i.e., 5 wt %) enhances the initial specific capacity of the NiS₂ microsphere electrodes to as high as 1605 mAh g⁻¹ at 0.1 A g⁻¹ current density, along with a drastic enhancement of rate capability and reversible specific discharge capacity (713.3 mAh g⁻¹) even after 120 cycles. Moreover, even after 120 cycles of charge−discharge cycling, the Coulombic efficiency of the electrode remains around 98.42%. The obtained results clearly demonstrate the advantages of the utilized synthesis strategy for fabricating porous metal sulfide microstructures for utilization as high-capacity anode materials for next-generation LIBs.

## ASSOCIATED CONTENT

**ⓈⓉ Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c00340.

> EDX analysis of the NiS₂:Mo microspheres; EDX mapping analysis; and SEM and TEM images of NiS₂:Mo microsphere electrodes after 120 cycles (PDF)

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**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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