Nanostructured polycrystalline Ni$_3$S$_2$ as electrode material for lithium ion batteries

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Keywords: powder vapor transport, nanostructured nickel sulphide, initially high-charging capacity, high capacity retention, Li$^{+}$ batteries

Abstract

We report the facile synthesis of nanostructured polycrystalline nickel sulphide (NP-Ni$_3$S$_2$) on Ni foil at 750 and 800 °C by employing powder vapor transport technique. X-ray diffraction patterns (XRD) confirms the formation of polycrystalline Ni$_3$S$_2$ phase with rhombohedral structure. Raman spectroscopy and x-ray photo-electron spectroscopy (XPS) further confirms the formation of Ni$_3$S$_2$ phase. Scanning electron microscopy (SEM) reveals the formation of flower shaped nanostructures of NP-Ni$_3$S$_2$ material. As an electrode material of Li$^{+}$ batteries, the initial discharge capacities for NP-Ni$_3$S$_2$ materials deposited at 750 and 800 °C are found to be ∼2649 mAh g$^{-1}$ and ∼1347 mAh g$^{-1}$, respectively with initial capacity loss of ∼1067 mAh g$^{-1}$ and ∼363 mAh g$^{-1}$ after first cycle and capacities of ∼931 mAh g$^{-1}$ and ∼818 mAh g$^{-1}$ after 30 cycles for a current density of 60 mA g$^{-1}$. An excellent capacity retention for NP-Ni$_3$S$_2$ material synthesized at 800 °C is due to its larger surface area and shorter diffusion length for mass and charge transport brought about by the flower–like porous nanostructures showing that the NP-Ni$_3$S$_2$ material synthesized at higher temperatures is more suitable as electrode material for Li$^{+}$ batteries.

1. Introduction

In this era of nanotechnology, extensive attention is being paid by the research community to develop effective energy storage devices due to the increasing demand for clean and renewable energy sources. Among them, due to the limiting availability of fossil fuels and associated environmental concerns, the electrochemical energy storage devices like Li$^{+}$ batteries and supercapacitors are expected to become more popular in near future. The performance of energy storage devices is associated with the nanostructures of synthesized materials especially their shape and size which have attained noteworthy attention both in fundamental and applied research areas [1–5].

Recently, Li$^{+}$ batteries have attracted huge attention for large-scale applications like full electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles because Li$^{+}$ batteries are the major power sources for transportable electronics. It is well known that the commercial graphite as electrode material exhibits low capacity (372 mAh g$^{-1}$) [6–9]. Compared to graphite, it is well known that the transition metal compounds have higher theoretical capacities and thus huge number of transition metal oxides has been widely used for Li$^{+}$ batteries with good electrochemical properties [10–15]. Thus, the growth of new nanostructured electrode materials with high capacity and energy density through cost-effective route is highly desirable.

Transition metal dichalcogenides (TMDs) have exhibited excellent electrochemical performance and become the excellent electrode materials for Li$^{+}$ batteries owing to their high capacities [16–18]. Cobalt sulphide...
and molybdenum disulphide nanostructured materials were used as electrode materials showed better discharge capacities and cycling performance [19, 20]. Porous nanostructured nickel sulphide, as electrode material, was fabricated on Ni foam and showed better discharge-charge capacities and cycling performance [21]. Lai et al [22] have developed a highly ordered large-scale Cu3S nanowires array as an electrode with a specific capacity of 145 mAh g\(^{-1}\). Ni et al [23] have synthesized a porous Ni3S2 nanostructured as an electrode material by employing hydrothermal route with discharge-charge capacities of 719 and 385 mA h g\(^{-1}\), respectively. Wang et al [24] have also developed porous Ni3S2/Ni nanoarchitectures film using the hydrothermal route and exhibited discharge-charge capacities of 535 and 451 mA h g\(^{-1}\). According to our knowledge, most of the research work on the deposition of TMDs films like copper sulphide, molybdenum sulphide and some work related to nickel sulphide films were done via hydrothermal and chemical vapor deposition routes, [23, 24]. Thus, there is a need to develop simple and cost-effective technique for the synthesis of such materials and thus more work is needed on the deposition of nickel sulphide material. Powder vapor transport (PVT) is a simple and efficient way of synthesizing TMDs materials with good properties and is opted in the present study.

In this paper, we use the PVT technique to synthesize nanostructured polycrystalline Ni3S2 (NP-Ni3S2) materials having flower-like nanostructures on Ni foil. A key attribute of this synthesis approach is the single-step dry-deposition of required electrode material and the electrochemical studies without further post growth assembly and manipulation. Remarkably, the NP-Ni3S2 nanostructured materials grown by PVT technique exhibited outstanding charge-discharge capacities. The discharge and charge capacities for NP-Ni3S2 material deposited at 750 °C are found to be 793 mAh g\(^{-1}\) and 389 mAh g\(^{-1}\) while for the material deposited at 800 °C, the capacities are 718 mAh g\(^{-1}\) and 798 mAh g\(^{-1}\) respectively after 30 cycles at the current density of 60 mA g\(^{-1}\). Results show that the single-step dry-synthesis of polycrystalline NP-Ni3S2 materials with flower like nanostructure can be used as electrode material for Li\(^+\) batteries.

2. Experimental details

2.1. Material synthesis

The NP-Ni3S2 materials are synthesized on Ni foil by employing PVT technique. Figures 2(A)–(C) shows the 3D/2D schematic and flow chart to illustrate the synthesis process of NP-Ni3S2 materials deposited on Ni substrates at 750 and 800 °C. The reactor is made up of quartz tube having diameter of ~40 mm and length ~70 cm. Two ceramic boats containing sulphur powder and Ni foil (substrate) are placed at ~16 cm apart inside the reactor; Ni substrate is located horizontally at the reactor centre whereas the sulphur powder is located at ~16 cm from the center such that the boats containing sulphur and Ni are at ~200 °C and ~750/800 °C. Firstly, the reactor is evacuated to the base pressure of 3 x 10\(^{-2}\) mbar with the help of rotary pump. A portable heater in the shape of a cylinder is used and placed at the centre of the cylindrical quartz tube (reactor). An inert gas (argon) with a flow rate of 100 sccm is used as the carrying gas to transport the sulphur vapor from one place to other inside the reactor. The reactor temperature is increased at the rate of 20 °C per minutes. The Ni foil (substrate) of diameter ~16 mm is used which is suitable to make cells by using steel coins of number 2016 for Li\(^+\) batteries performance test. When the reactor temperature at its center is ~750/800 °C, the reactor temperature at ~16 cm away from the center is at ~200 °C where the sulphur in the form of powder is placed. The sulphur powder gets enough energy resulting in bonds breaking and hence evaporation. The evaporated sulphur vapor are carried towards hot Ni substrate with the help of argon gas with the flow rate of 100 sccm which strikes the hot substrate surface which is already at ~750 or 800 °C. The evaporated sulphur species striking the hot surface of Ni substrate react with Ni atoms to form the NP-Ni3S2 material.

We hypothesize that the structural, morphological, compositional and electrochemical properties of NP-Ni3S2 materials are associated with the energy flux of sulphur vapor striking the substrate surface and the reaction rate between the involved species; sulphur and Ni atoms, at the hot surface of Ni substrate. The energy flux of sulphur vapor striking the hot surface of the Ni substrate depends on the flow rate of carrier gas. The growth mechanism of NP-Ni3S2 Material synthesized by PVT technique can be understood from the following kinetic equations.

\[
\text{Ni} + \text{S} \rightarrow \text{NiS} \\
3\text{Ni} + 2\text{S} \rightarrow \text{Ni}_3\text{S}_2
\]

These kinetic equations show that two types of nickel sulphide (NiS or Ni3S2) may be formed during the synthesis process and their formation is associated with the change in energy flux and reaction rate between the constitutes at the hot surface of Ni substrate. The energy flux of the evaporated sulphur species striking at the hot substrate surface is more as the temperature of substrate is increased because hotter substrate surface may attract larger number of evaporated sulphur species to react. The flux of evaporated sulphur species reaching the hot substrate surface also depends on the flow rate of carrier gas. Therefore, the flux of evaporated sulphur species reaching the hot substrate surface, the reaction rate between the sulphur and Ni species and flow rate of carrier...
Gas are responsible to change the structural, morphological and hence electrochemical performance of NP-Ni₃S₂ materials.

### 2.2. Characterization techniques

The synthesized NP-Ni₃S₂ materials are characterized by using x-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS) to study the structural, morphological and compositional properties whereas the electrochemical measurements are performed to confirm the use of synthesized NP-Ni₃S₂ as electrode material for Li⁺ batteries. Lithium metal foil of thickness (0.59 mm) is used as the counter electrode whereas 1 M solution of LiPF₆ in ethylene carbonate and diethyl carbonate is used as the electrolyte. The polypropylene foil is used as a separator between the electrodes. Coin-type test cell of size 2016 is fabricated in a glove box filled with argon gas. It is to be noted that no binder or conducting carbon is mixed with NP-Ni₃S₂ material for the fabrication of working electrode. The geometrical area of the electrode is found to be 2.0 cm². The active mass of the synthesized NP-Ni₃S₂ materials is calculated using, \( M_a = M_t - M_b \) where \( M_a \), \( M_t \) and \( M_b \) are the active mass of working electrode, total mass of substrate after deposition and mass of substrate before deposition respectively. A scientific electronic balance is used to measure the weight of the Ni substrate (before and after deposition). The active mass of NP-Ni₃S₂ materials deposited at 750 °C and 800 °C is found to be \(~1.6\) and \(~1.9\) mg, respectively. The fabricated cells are placed in a fume hood overnight before the measurements. The galvanostatic discharge-charge cycling and cycling voltammetry are carried out at room temperature by using multichannel battery tester (model SCN, Bitrode, USA) and Maepile II system (Biologic, France) respectively.

### 3. Results and discussion

#### 3.1. Structural analysis

Morphology of the synthesised NP-Ni₃S₂ materials is investigated using SEM analysis. Figures 2(A), (B) show the SEM nanostructures of NP-Ni₃S₂ materials after 20 min growth on Ni substrates at 750 and 800 °C. Figure 2(A) shows that the NP-Ni₃S₂ material grown at 750 °C consists of nanoparticles and their agglomerates, whereas the NP-Ni₃S₂ material synthesized at higher temperature of 800 °C, in figure 2(B), is comprised of much greater...
number of nanoparticle agglomerates assembled in flower like porous nanostructures. Careful look reveals that the flower like nanostructures may consist of nanorods, horizontal sheets and nanoparticles. It is obvious that the nanostructure of NP-Ni3S2 material obtained at lower temperature is more compact than the nanostructure of NP-Ni3S2 material observed at higher temperature. The porous nature of nanostructure of NP-Ni3S2 material at higher temperature is more favourable for electrochemical performance due to its more accessibility into electrolytes and hence is expected to increase the reaction rate between NP-Ni3S2 material and electrolytes and hence would enhance the electrochemical performance of the material under test.

Table 1 shows the various structural parameters and their comparison with the standard values which help us to understand the crystal structure of NP-Ni3S2 materials. Moreover, the development of multiple diffraction peaks related to rhombohedral NP-Ni3S2 phase confirms the synthesis of NP-Ni3S2 materials for both temperatures. The small shift in the diffraction peaks indicates the presence of residual stresses. The shifting of diffraction peaks is associated with the increase of temperature as well as the diffusion of oxides interstitially or reaction with Ni atoms to form NiO phase. The calculated values of d-spacing for various diffraction planes are in good agreement with the standard values. The values of crystallite size of (110) plane are found to be 63.6 and 85.6 nm when the NP-Ni3S2 films are synthesized at 750 and 800 °C temperature respectively. The development of diffraction peak related to NiO phase comes from the reaction between Ni and native oxides generated during
high temperature synthesis process. However, NiO phase is in small quantity as its peak intensity is smaller. The crystal structure of the synthesized NP-Ni$_3$S$_2$ materials is further investigated by Raman spectroscopy. Figure 3(B) shows the micro-Raman spectrum measured at room temperature of the NP-Ni$_3$S$_2$ materials synthesized at 750 and 800 °C. Raman spectra shows the appearance of two Raman bands centred at 304 and 348 cm$^{-1}$. The factor group analysis based on the correlation method revealed that the irreducible representation (G) of phonon modes for rhombohedral Ni$_3$S$_2$ phase (space group R32 (155) material is

\[
G^{\text{Ni}_3\text{S}_2\text{crystal}} = 2A_1^R + 2A_2^R + 4E^{R,IR},
\]

in which there are 6 Raman active modes, in total, centred at 185, 197, 218, 302, 320, and 348 cm$^{-1}$. These Raman active bands are ascribed to the vibration modes of the rhombohedral Ni$_3$S$_2$ phase [17, 25]. In our case, the two Raman vibration bands centred at 304 and 348 cm$^{-1}$ for both substrate temperatures are very close to the literature values and thereby confirming the synthesis of rhombohedral NP-Ni$_3$S$_2$ materials.

### 3.2. Electrochemical performance

The electrochemical performance of NP-Ni$_3$S$_2$ materials synthesized at different (750 and 800 °C) temperatures as electrode for Li$^+$ batteries are investigated by using galvanostatic charging-discharging cycles and cyclic voltammetry. Figures 4(A), (B) exhibits the charging-discharging cycles of NP-Ni$_3$S$_2$ material synthesized at 750 and 800 °C temperature respectively. The charging-discharging cycles is carried out in the potential window of 0.005–3.0 V versus Li/Li$^+$ at the current density of 60 mA g$^{-1}$. The open circuit voltages (OCV) of fabricated aged (overnight) cells of NP-Ni$_3$S$_2$ materials synthesized at 750 and 800 °C temperatures are found to be ~2.75 and ~2.92 V respectively. In the first discharge cycle, two larger voltage plateaus at ~0.79, ~0.45 and ~0.97 and ~0.71 V showing a complicated shape, following by sloping curves with total first discharge capacities of ~2649 ± 5 and ~1344 (mAh)/g while in the first charging cycle, two elegant voltage plateaus at ~1.91, ~2.28 and ~1.86, ~2.21 V following by sloping curves with total charging capacities of ~1573 ± 5, ~993 ± 5 (mAh)/g for NP-Ni$_3$S$_2$ electrode materials (synthesized at 750 and 800 °C) respectively are obtained. Noticeably, the charging-discharging capacities of NP-Ni$_3$S$_2$ electrode material synthesized at lower temperature is more than the NP-Ni$_3$S$_2$ electrode material synthesized at higher temperature respectively. It is found that the plateau voltages in the subsequent discharge cycles are shifted to higher values ~1.41, ~1.36, ~1.26 and ~1.47, ~1.45, ~1.43 V for 2nd, 10th and 20th cycles for the NP-Ni$_3$S$_2$ electrode materials synthesized at 750 and 800 °C temperatures respectively. A small change in voltage plateaus in the subsequent charging cycles for the NP-Ni$_3$S$_2$ electrode material synthesized at 750 °C is observed while the voltage plateaus in the subsequent charging cycles for the NP-Ni$_3$S$_2$ electrode material synthesized at 800 °C is shifted to lower values. In short, the shape and width of voltage plateaus of the subsequent charging-discharging curves for the electrode (NP-Ni$_3$S$_2$) materials synthesized at various temperatures and from the first charging-discharging cycles which agrees with the reported values [17]. These initial charging-discharging capacities of NP-Ni$_3$S$_2$ electrode materials synthesized at various temperatures are much higher than the reported values (596 and 466 mAh g$^{-1}$) of nickel sulphide nanostructured film respectively. Moreover, in our case, the charging-discharging capacities (~1181 ± 5, ~1159 ± 5 and ~818 ± 5, ~798 ± 5) of NP-Ni$_3$S$_2$ electrode materials synthesized at 750 and 800 °C after 20 cycles respectively are much higher than the charge capacity (~466 mAh g$^{-1}$) of nickel sulphide nanostructured film [17]. Markedly, the charging-discharging capacities of NP-Ni$_3$S$_2$ electrode material synthesized at lower temperature are higher than the electrode material synthesized

| Deposition temperature | Phases   | (2θ)$^\circ$ | (2θ)$^\circ$ standard | FWHM | Peak intensity (arb-unit) | d-spacing-observed | d-spacing-standard |
|------------------------|----------|--------------|------------------------|------|--------------------------|-------------------|-------------------|
| 750 °C                 | NiS$_2$  | 10 1         | 21.76                  | 0.132| 223.6                    | 4.0874            | 4.0810            |
|                        |          | 11 0         | 31.12                  | 0.144| 552.51                   | 2.8709            | 2.8734            |
|                        |          | 00 3         | 37.86                  | 0.137| 162.64                   | 2.3736            | 2.3781            |
|                        |          | 02 1         | 38.40                  | 0.066| 60.51                    | 2.3411            | 2.3493            |
|                        |          | 20 2         | 44.52                  | 0.135| 25.47                    | 2.0327            | 2.0880            |
|                        | NiO      | 20 0         | 43.36                  | 0.109| 335.51                   | 2.0845            | 2.0404            |
| 800 °C                 | NiS$_2$  | 10 1         | 21.85                  | 0.082| 223.31                   | 4.0633            | 4.0810            |
|                        |          | 11 0         | 31.14                  | 0.107| 1095.88                  | 2.8688            | 2.8734            |
|                        |          | 00 3         | 37.87                  | 0.062| 290.59                   | 2.3729            | 2.3781            |
|                        |          | 02 1         | 38.38                  | 0.068| 66.87                    | 2.3426            | 2.3493            |
|                        |          | 20 2         | 44.49                  | 0.194| 25.87                    | 2.0388            | 2.0880            |
|                        | NiO      | 20 0         | 43.38                  | 0.207| 117.43                   | 2.0833            | 2.0404            |
at higher temperature even after 20 cycles. Such a high Lithium storage capacity along with nanophase NP-Ni3S2 material is also associated with the formation of solid electrolyte interphase (SEI) layer [17, 23, 24, 26].

Figures 4(C), (D) shows the capacity retention of NP-Ni3S2 electrode material synthesized at 750, 800 °C temperatures. It is found that the charging-discharging capacities of NP-Ni3S2 electrode materials synthesized at 750 and 800 °C are found to be ~931 ± 5, ~910 ± 5 and ~818 ± 5, ~798 ± 5 mAh g⁻¹ respectively after 30 cycles which may be due to the limited access of electrolyte/active material and unaccommodating strains produced during the electrochemical reaction. The irreversible capacity loss (ICL) during first charging-discharging cycle for the NP-Ni3S2 electrode material synthesized at 750, 800 °C is found to be ~1076 and ~363 (mAh)/g respectively which arises due to incomplete decomposition of SEI and Li2S, intrinsic nature of NP-Ni3S2 electrode material, flower like nanostructure and kinetic limitations [5, 27–29]. Obviously, the cyclic stability is not good, but the values of discharge-charge capacities are much higher than the previously reported values of NP-Ni3S2 electrode material [17]. This lower cyclic stability of NP-Ni3S2 electrode material may be due to the limited stability of sulphides and packed nanostructural morphology containing agglomerates and hence limit the access of electrode material to electrolyte significantly.

The cyclic stability of NP-Ni3S2 electrode materials exhibited excellent electrochemical behaviour which is undoubtedly due to the intrinsic characteristics of NP-Ni3S2/Ni electrode material which is already described by the formation of flower like nanostructured porous material because these nanostructured features can provide good access to electrode material to the electrolyte significantly. It is found that the charging-discharging capacity and ICL of NP-Ni3S2 electrode material synthesized at lower (750 °C) temperature is more than the charging-discharging capacity and ICL of NP-Ni3S2 electrode material synthesized at higher (800 °C) temperature. Results show that the NP-Ni3S2 electrode material synthesized at higher temperature is more favourable as electrode material for Li⁺ batteries.

Figure 5 shows the cyclic voltammograms of NP-Ni3S2 electrode material synthesized at higher (800 °C), for first 6 cycles, in the potential window of 0.005–3.0 V versus Li⁺/Li and a scan rate of 0.1 mVs⁻¹. In the initial cathodic scan, two reduction peaks at ~1.06 and ~1.19 V indicate the reduction of Ni₃S₂ phase into Ni and the
formation of SEI film while in the initial anodic scan, two oxidation peaks located at $\sim 1.98$ and $\sim 2.25$ V are attributed to the decomposition of Li$_2$S and the formation of Ni$_3$S$_2$ phase, respectively. An obvious difference between the first and subsequent five cycles is that the cathodic peaks are shifted towards higher potential ($\sim 1.09$ and $\sim 1.32$ V) owing to the material activation [17, 21, 23, 30–32]. It is obvious that a pair of redox peaks ($\sim 1.09$ and $\sim 1.98$ V) is maintained corresponding to the charging-discharging plateaus at $\sim 1.86$ V and $\sim 0.97$.

The basic electrochemical reactions for nickel sulphide material in Li$^+$ battery can be understood by the following kinetic equations:

$$\text{Ni}_3\text{S}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow 3\text{Ni} + 2\text{Li}_2\text{S}$$

$$\text{Ni}_3\text{S}_2 + 4\text{Li} \leftrightarrow 3\text{Ni} + 2\text{Li}_3\text{S}$$

This electrochemical reaction mechanism is based on the XRD, Raman and XPS analysis which indicate the formation of rhombohedral polycrystalline Ni$_3$S$_2$ phase. Table 2 shows the comparison between the charging-discharging capacities of present and previously work [17,23–25]. The electrochemical measurements of the present work indicate that the charging-discharging capacities of Ni$_3$S$_2$ electrode material showing flower like morphology are improved when deposited by a simple PVT technique.

The coulombic efficiency, an important parameter in the characterization of energy storage devices, for NP-Ni$_3$S$_2$ as electrode material synthesized at 750 and the 800 °C temperatures is found to be $\sim 98$%–$99$%. Result shows that the capacity fading is more for the NP-Ni$_3$S$_2$ material synthesized at lower temperature which is decreased significantly when it is synthesized at higher temperature. The capacity retention is more for the NP-Ni$_3$S$_2$ material synthesized at higher temperature which is decreased significantly when it is synthesized at lower temperature. The inverse relation between the capacity fading and capacity retention with the increase of

Table 2. Shows the comparison between the charging-discharging capacities of present and previous work.

| Electrode materials                          | 1st charge-discharge capacity (mAh g$^{-1}$) | References |
|-----------------------------------------------|---------------------------------------------|------------|
| Ni$_3$S$_2$/Ni nanostructured material        | 535/451                                     | [23]       |
| Ni$_3$S$_2$/Ni nanoarchitected material       | 719/385                                     | [24]       |
| Ni$_3$S$_2$ nanowire array                    | 480/430                                     | [25]       |
| Ni$_3$S$_2$ thin film                         | 350/330                                     | [25]       |
| Ni$_3$S$_2$ carpet like nanostructure          | 596/466                                     | [17]       |
| Ni$_3$S$_2$/Ni flower shaped nanostructured material | 2649/1573 750 °C [first cycle] and 1347/984 800 °C | Present work |
|                                              |                                             | 931/910 750 °C [30th cycle] 818/798 800 °C |

Figure 5. Cyclic voltammograms (current versus potential) of NP-Ni$_3$S$_2$ electrode material synthesized at 800 °C temperature.

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synthesizing temperature is due to the nanostructural change from more compact nature of nanoparticles to flower like porous nanostructure. This shows that the synthesized NP-Ni$_3$S$_2$ material is an efficient electrode material for Li$^+$ battery.

3.3. XPS analysis

Result shows that the electrochemical performance like charging-discharging cycles, capacity retention and coulombic efficiency up to 30 cycles for the NP-Ni$_3$S$_2$ material synthesized at higher (800 °C) temperature is good. Therefore, the XPS analysis of NP-Ni$_3$S$_2$ material synthesized at higher temperature is performed to investigate the binding energy and oxidation states. Figure 6 shows the core levels XPS spectra of Ni (2p), S (2p), O (1s) and C (1s) present in NP-Ni$_3$S$_2$ material synthesized at higher temperature. All core levels spectra are calibrated with the binding energy of C-1s (284.6 eV) core level. Figure 6(A) shows that the XPS Ni-2p spectrum consists of two regions ranged from 852–868 eV and 870–885 eV. The XPS peaks centred at ∼854.5, ∼861.5 and ∼873 and ∼880 eV are attributed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ spin–orbit levels respectively, thereby confirming the synthesis of Ni$_3$S$_2$ phase while the satellite peaks centred at ∼857.47 and ∼875.9 eV confirm the formation of Ni nanoparticles [33–37]. Figure 6(C) shows the broad XPS O-1s spectrum (ranged from ∼528 to ∼533 eV) of NP-Ni$_3$S$_2$ material. The peaks centred at ∼529 and ∼530 eV are attributed to oxygen which reacts with Ni$^{2+}$ to form NiO phase due to surface oxidation. Figure 6(B) shows that the XPS S-2p spectrum consists of different peaks centred at ∼162.2, ∼163.2, ∼163.8, ∼164.6, ∼165.7, ∼168.8, and ∼169.9 eV respectively. The XPS peaks centred at ∼162.2, ∼163.2 eV and ∼163.7, ∼164.6 eV are ascribed to S 2p$_{3/2}$ and S 2p$_{1/2}$ spin–orbit levels respectively and confirms the presence of S$^{2-}$ in Ni$_3$S$_2$ material [38–40]. The peak centred at ∼163.2 eV corresponds to metal-sulphur (Ni–S) bonds while the peak centred at ∼162.2 eV is ascribed to sulphur ions at low coordination numbers on the surface [41–43]. The peaks centred at ∼168.8 and ∼169.9 eV are ascribed to surface oxidation of Ni$_3$S$_2$ compound [44]. The XPS results thus further confirm that the evaporated S$^{2-}$ reacts Ni$^{2+}$ to form nickel sulphide phase.

Figure 6. XPS spectra of NP-Ni$_3$S$_2$ material synthesized at higher temperature show the core levels of (A) Ni-2p, (B) S-2p, (C) O-1s, (D) C-1s.
4. Conclusions

The NP-Ni$_3$S$_2$ materials are synthesized on Ni foils by using simple, dry and cost-effective PVT technique. The NP-Ni$_3$S$_2$ material synthesized at lower (750 °C) temperature is more compact while it shows flower like porous nanostructure when synthesized at higher (800 °C) temperature. The XRD, Raman and XPS analysis confirms the synthesis of rhombohedral NP-Ni$_3$S$_2$ materials. The electrochemical performance of NP-Ni$_3$S$_2$ materials synthesized at 750 and 800 °C temperatures exhibits the charging-discharging capacities of ~931 ± 5, ~910 ± 5 and ~818 ± 5, ~798 ± 5 mAh g$^{-1}$ after 30 cycles at the current density of 60 mA g$^{-1}$, respectively. The charging-discharging capacity of NP-Ni$_3$S$_2$ material synthesized at lower temperature is more than the charging-discharging capacity of NP-Ni$_3$S$_2$ material synthesized at higher temperature. The capacity fading is more for the NP-Ni$_3$S$_2$ material synthesized at lower temperature which is decreased significantly when the electrode material is synthesized at higher temperature. The capacity retention is more for the NP-Ni$_3$S$_2$ material synthesized at higher temperature which is decreased significantly when it is synthesized at lower temperature. The inverse relation between the capacity fading and retention with the increase of synthesizing temperature is due to the nanostructural change from more compact to porous nanostructure. In short, the achievement of excellent charging-discharging capacity, capacity retention and coulombic efficiency is due to its larger surface area exposed to electrolyte and shorter diffusion layer for mass and charge transport. The simplicity of synthesis methodology and the better electrochemical performance make the synthesized NP-Ni$_3$S$_2$ a promising electrode material for Li$^+$ batteries.

Funding

This work is supported by the Punjab Higher Education Commission (PHEC) Pakistan under the education enhancement project entitled ‘Scholarship for POSTDOC Study’ for various Universities of Punjab, Pakistan. One of the authors (I A Khan) is grateful to the PHEC for providing financial support during his POSTDOC studies at National Institute of Education, Nanyang Technological University Singapore.

Declaration of interest

None.

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