

Preparation of NiS₂ Using Spark-Plasma-Sintering Process and Its Electrochemical Properties

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Single-phase NiS₂, which was hardly prepared by conventional processes such as mechanical milling or precipitation reaction, was prepared using the spark plasma sintering (SPS) process. Using porous Ni (porosity 95%) as a starting material, similar-shaped porous NiS₂ (porosity 89%), containing trace amounts (ca. 3%) of NiS, and finally single-phase NiS₂ powder were obtained by the SPS process. The electrochemical tests demonstrated that the present NiS₂ samples showed the initial discharge capacity of ca. 820 mAh g⁻¹, which was ~94% of the theoretical value. The capacity retention after 10 cycles was ca. 19%, and such rapid degradation was mainly attributable to the irreversibility of the Li extraction from the lithiated (discharged) NiS₂ electrodes and the electrical disconnections among the active materials, carbon powders, and/or current collectors. © 2008 The Electrochemical Society. [DOI: 10.1149/1.2953496] All rights reserved.

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Sulfur and metal sulfides are promising cathode materials for high-energy rechargeable lithium batteries because of their high theoretical capacities and relatively low costs.¹⁻¹⁰ Elemental sulfur is both electronically and ionically resistive, which gives rise to low active material utilization and poor rechargeability in Li/S cells with liquid electrolytes.² Metal sulfides (MS_x) showed relatively higher electronic conductivity and higher utilization in the Li/MS_x system, and a variety of metal sulfides, such as M = Ti, Mo, Cu, Ni, and Fe, have been studied.^{1,4-10} Among them, Jasinski and Burrows first reported that nickel sulfide could be used as a cathode material for rechargeable lithium batteries.⁷ They carried out the electrochemical tests for $Ni_3S_2,\ Ni_6S_5,\ Ni_7S_6,\ NiS,\ Ni_3S_4,\ and\ NiS_2$ in LiClO₄-propylene carbonate electrolyte, and the highest utilization was obtained for Ni₃S₂, though the materials with high sulfide content (NiS₂) should theoretically provide a high specific capacity value. This discrepancy would be partly originated from the low quality of the samples; the purity and homogeneity of the nickel sulfides prepared early by thermosynthesis and the chemical process was unsatisfactory.^{4,7,8} Recently, Han et al. prepared single phase NiS by mechanical alloying and reported that it showed the initial discharge capacity of 580 mAh g^{-1} , which was ca. 90% of the the-oretical value (645 mAh g^{-1}).⁸⁻¹⁰ Preparation of other single-phase nickel sulfides, such as Ni_3S_2 , as well as their electrochemical properties, was also reported recently,^{4,11} but there have been very few studies on NiS₂. This would be due partly to the difficulty of the preparation of single-phase NiS₂.

Metal sulfides were traditionally prepared by the thermal reactions of the component metal powders and sulfur in evacuated silica tubes at high temperatures or by the reaction of hydrogen sulfide gas with the aqueous solution of the metal salts.^{12,13} The low melting point (ca. 120°C) and volatilization of sulfur generally makes the control of composition difficult with these reactions. Because these traditional preparation methods involved complicated operational processes, such as high-temperature treatment of the sealed samples for longer time or handling of toxic H₂S gas, alternative preparation routes have been studied. Recently, a low-temperature synthesis procedure has been developed and several nickel sulfides, such as Ni₃S₂, Ni₃S₄, and NiS, have been prepared by precipitation reactions or hydrothermal synthesis.¹²⁻¹⁴ However, the single phase with higher sulfur content, that is NiS₂, has not yet been reported thus far, and therefore, its electrochemical property has not yet been clarified up to date.

Spark plasma sintering (SPS) is a process that makes use of microscopic electrical discharge between particles under the reductive atmosphere.¹⁵⁻¹⁷ This process enables the sample powders, en-

closed in the graphite die, to be heated in a relatively short time as compared to the conventional heating in the muffle furnace. The short heating time and enclosure in the graphite die used in the SPS process would be advantageous in suppressing the flowing out of the sulfur vapor outside, resulting in making the control of composition easier and simplifying the preparation process. In addition, the reductive SPS conditions would be effective to suppress the oxidation of metal sulfides during heating.

In the present work, we tried to prepare single phase NiS_2 using the SPS process in a more simplified manner as compared to the traditional methods. The electrochemical properties of the obtained NiS_2 were also examined.

Experimental

Our present methodology is schematically shown in Fig. 1. The elemental nickel and sulfur were loaded into the graphite die, and a pulsed dc current (ca. 1000 A) was applied to it in the chamber filled with argon gas, which generated the heating of the graphite die and promoted the reactions under the sealed atmosphere. When nickel and sulfur powders were used as starting materials, Fig. 1b, the sulfur vaporized and the nickel powder went downward after heating the graphite die. This was ineffective for the reaction because of the small specific area for both starting materials to encounter, and it took a long time to complete the reaction, as in the traditional methods. Instead, we used sponge-shaped porous Ni as the starting material (Fig. 1a). In this procedure, the initial Ni still kept



Figure 1. Schematic representation of the preparation process by the SPS method using (a) Ni sponge and (b) Ni powder.

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the original shape even after the sulfur vaporized by heating, which resulted in the promotion of the sulfurizing reaction due to its larger specific area. In addition, the pulsed dc current partly passed through the porous Ni during the SPS process, which gave rise to the heating of Ni itself. This was effective for heating more homogeneously inside the graphite die, and also assisted in promoting the reaction.

Using the above techniques, we tried to prepare single-phase NiS₂. Before the SPS treatment, the sponge-shaped porous Ni (porosity 95%, Sumitomo Electric Industries, Ltd., Japan) was washed by immersing in 1 M HCl solution. This Ni sponge was placed in a graphite die (15 mm diam) with excess amounts of elemental sulfur powder (molar ratio Ni:S = 1:40). After the graphite die was equipped in the SPS apparatus (SPS-3.20 MK-IV, SPS Syntex Inc., Japan),¹⁵⁻¹⁷ the system was evacuated down to ca. 20 Pa and then filled with argon gas, followed by applying a dc electric current of ca. 1000 A to pass through the graphite die. During this procedure, the temperature was increased up to 600°C at a rate of 10°C min⁻¹ (controlled by the applied current). After it was kept at 600°C for 10 min, the current was switched off and the sample was cooled to room temperature. The resulting porous material was again placed in the graphite die with the same amounts of sulfur powder and underwent the same SPS treatment. After it was repeated for four times to promote the sulfurizing reaction, the resulting porous product was finally ground and blended with the half amounts of the initial sulfur powder, followed by the same SPS treatment to obtain single-phase NiS₂ powder.

The phase purity of the sample was checked by X-ray diffraction (XRD) measurement (Rotaflex RU-200B/RINT, Rigaku) using monochromatic Cu K α radiation within the 2 θ ranges of 10–125 °. The RIETAN-2000 program was used for structural refinement with X-ray Rietveld analysis.¹⁸ The porosity of the sponge-shaped product was measured using the Archimedes method. The particle size distribution of the powder samples was measured by laser diffraction and scattering method (AEROTRAC SPR, model no. 7340, Nikkiso). Morphology of the samples was examined by scanning electron microscopy [(SEM), Rigaku JSM-6390LA]. Valence states of Ni and local structures around Ni atoms of the samples were examined by Ni K-edge X-ray absorption fine structure (XAFS), which were obtained in the transmission mode with an X-ray spectrometer (EXAC-820, Technos). The X-ray generator with a Mo rotating anode and a LaB₆ cathode was operated at a voltage of 20 kV and a current of 200 mA. The incident X-ray beam was monochromatized with a Ge(220) Johanson curved crystal. The intensity of the X-ray beam was measured by a sealed-type proportional counter and a solid-state detector for the incident and the transmitted X-ray, respectively. The obtained XAFS spectra were analyzed using the TECHXAS-SW Version 3.0 program package (Technos). The electrochemical lithium insertion/extraction reactions were carried out using lithium coin-type cells. The working electrode consisted of a mixture of a 5 mg NiS₂ and a 5 mg acetylene black powder with a 0.5 mg Teflon powder pressed into a 15 mm diam tablet under a pressure of 10 MPa. The electrochemical test cells were constructed in a stainless steel coin-type configuration. The negative electrode was a 15 mm diam and 0.2 mm thick disk of Li foil, and the separator was a microporous polyolefin sheet. The solution of 1 M LiPF₆ in a 50:50 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) by volume (Tomiyama Pure Chemical Industries Ltd., battery grade) was used as the electrolyte. Cells were constructed in an argon-filled glove box, and the electrochemical measurements were carried out at 30°C initially with discharging, after standing overnight on open circuit, using a TOSCAT-3100 (Toyo System) at a current density of 175 mA g^{-1} (0.2 C) between 3.0 and 1.0 V. To check the amount of sulfur dissolved in the form of polysulfides in the electrolyte during the electrochemical tests, sulfur contents in the electrolytes, as well as fluorine contents for references, were measured by ion chromatography (ICA2000, DKK-Toa Co.) after the initial discharging and charging of the cells.



Figure 2. SEM images for (a) the sponge-shaped porous Ni used as the starting material, (b) the SPS-treated porous NiS₂ product containing trace amounts (ca. 3%) of NiS, (c) the SPS-treated single-phase NiS₂ powder, and (d) the mechanically milled NiS₂ powder.

Results and Discussion

The SPS-treated (at 600°C) porous product was dark gray in appearance, and the measured porosity was ca. 89%, which was slightly lower than that (ca. 95%) of the initial Ni sponge. Figures 2a and b show the typical SEM images of the initial Ni sponge and the SPS-treated porous product. The initial Ni sponge consisted of ten to several tens of micrometer-diameter wires with several hundreds of micrometer-sized pores. After the SPS treatment with sulfur, each wire broadened and the pores were reduced in size, which suggests that the sulfur incorporated into Ni and reacted to form nickel sulfides. Figure 3a shows the XRD pattern of the SPS-treated (at 600°C) porous product. Most of the XRD peaks (denoted as open circles) were indexed by the cubic unit cell $(Pa\overline{3})$, and the estimated lattice parameter [a = 5.68881(8) Å] was consistent with that [a= 5.6873(5) Å] reported previously for NiS₂.¹⁹ Other small peaks (denoted as closed triangles) were assigned to NiS,²⁰ and its content was estimated to ca. 3% by the X-ray Rietveld analysis using the RIETAN-2000 program.¹⁸ We also carried out the SPS treatment at 400–500 and $700-1000\,^{\circ}\mathrm{C}$ under the same condition, and each sample showed more amounts of NiS content as compared to that of the SPS-600°C samples; the SPS treatment at 600°C was the most favorable condition in the present procedure. The present optimal SPS temperature, 600°C, would be specified by balancing two con-



Figure 3. XRD patterns (Cu K α radiation) for (a) the SPS-treated porous NiS₂ product containing trace amounts (ca. 3%) of NiS, (b) the SPS-treated single-phase NiS₂ powder, and (c) the mechanically milled NiS₂ powder.

flicting factors of (*i*) the promotion of sulfurizing reaction of Ni sponge to form NiS₂ and (*ii*) the decomposition of NiS₂ at elevated temperatures. Thus, sponge-shaped porous products consisted mostly of NiS₂ were prepared by the present SPS process.

In order to obtain single-phase NiS₂, the above porous product (prepared by five-time repetitive SPS treatment) was ground and underwent the same SPS treatment after being blended with sulfur powder. The resulting powder was similar dark gray in color, and its XRD pattern is shown in Fig. 3b. All peaks were assigned to NiS₂, and any impurity peaks were not detected. The estimated lattice parameter was a = 5.68829(5) Å, which was again consistent with the previously reported value $[a = 5.6873(5) \text{ Å}]^{.19}$ Thus, the sulfurizing reaction was further promoted and completed by increasing the specific surface area, and finally, single-phase NiS₂ powder was obtained. Single-phase NiS_2 powder was also obtained by the SPS treatment after blending sulfur powder with the ground porous product prepared by the single SPS treatment of Ni sponge and sulfur; totally, two-time SPS treatment was enough to obtain single-phase NiS₂ powder, though five-time repetitive SPS treatments were carried out in the above procedure for obtaining the porous product with higher NiS₂ content.

The measured weight gain of the final product NiS₂ against the initial Ni sponge was ca. 104%, which is consistent with the ideal value (ca. 109%) assuming the reaction Ni + 2S \rightarrow NiS₂. Therefore, the excess amounts of the initial sulfur (S/Ni = 40) vaporized and mostly escaped from the graphite die during the SPS process, and seemed not to remain as an amorphous phase in the final product NiS₂. This would be originated from the incomplete sealing of the graphite die in the present procedure (Fig. 1); modifying the shape of the graphite die to improve its sealing might diminish the amounts of the sulfur powder required for obtaining single-phase NiS₂.

The typical SEM image for the present NiS₂ powder is shown in Fig. 2c. The sample powder consisted of mainly micrometer-sized primary particles (much smaller than the wire diameter of the porous product, Fig. 2b), and they formed agglomerates with the size of ca. 10 μ m. The laser diffraction and scattering measurements showed that the averaged particle size of the present NiS₂ powder was ca. 9.2 μ m, which is consistent with the size of the agglomerates.

In order to examine the validity of the above preparation process, we also carried out the SPS treatment (*i*) under the atmospheric air condition using the Ni sponge and the sulfur powder as starting materials and (*ii*) under the argon atmosphere using nickel and sulfur powders. In both cases, gray-colored powders were obtained and their XRD patterns showed that they consisted of mainly NiS. These results suggest that the sulfurizing reaction did not proceed to the final product NiS₂, probably due to (*i*) the lack of sufficient sulfur vapor inside the graphite die by the oxidation of sulfur during the SPS treatment or to (*ii*) the smaller reaction surface area as shown in Fig. 1b. Therefore, both the nonoxidative atmosphere and the porous Ni are necessary to obtain single-phase NiS₂ more efficiently using the SPS process.

Figure 4 shows the initial, second, and third discharge and charge curves for the cells with the present single-phase NiS₂ sample. The initial discharge capacity was ca. 820 mAh g⁻¹, which was ~94% of the theoretical value (ca. 870 mAh g⁻¹) assuming an electrochemical reaction NiS₂ + 4Li \rightarrow Ni + 2Li₂S. Jasinski and Burrows reported that NiS₂ was discharged to 1.5 V with the utilization of ca. 23% (corresponding to ca. 200 mAh g⁻¹) in LiClO₄-propylene carbonate electrolytes.⁷ Their reported discharge capacity was lower than our present result (ca. 440 mAh g⁻¹ at 1.5 V, Fig. 4), though the cell components and the electrochemical test conditions were different to ours. This would be partly originated from the presence of impurity in their samples; they precipitated NiS₂ from aqueous solution, which could result in the contamination of elemental sulfur in the samples, leading to its dissolution in the electrolytes during the electrochemical tests.^{4,7,8}



Figure 4. Initial, second, and third discharge and charge profiles for the single-phase NiS₂ sample cells at 175 mA g^{-1} (0.2 C). Notations A–G correspond to those in Fig. 5.

The present single-phase NiS₂ sample cells showed drastic capacity degradation with cycling (Fig. 4). A notable point is that the capacity values decreased mainly during charging after the preceding discharging; for example, the initial and second charge capacities were ca. 600 and 400 mAh g⁻¹, which were about 73 and 71% of the initial and second discharge capacities, respectively, while the second and third discharge capacities (ca. 560 and 400 mAh g⁻¹) were nearly consistent with the initial and second charge capacities. In addition, the decrease in charge capacity seems to be attributed to the fading of higher voltage plateaus (ca. 2.2 and 2.7 V), though the lower voltage plateau (ca. 1.9 V) remained almost unchanged. This would correspond to the fading of a higher voltage plateau (ca. 1.7–1.8 V) during discharging, with a lower voltage plateau (ca. 1.4 V) maintained at a similar length.

In order to examine the structural changes of NiS_2 during electrochemical cycling, we disassembled the Li/NiS₂ cells after cycling to the selected state of charge or discharge, washed the positive electrodes with DMC to remove the electrolyte, and carried out ex situ XRD and XAFS measurements for them. Figure 5 shows the ex situ XRD patterns for the initial positive electrode and those with different states, denoted in Fig. 4, during cycling. In the first discharge, sharp peaks ascribed to NiS₂ reduced in intensity and finally were not observed at the end of it (B). This indicates that the initial



Figure 5. Ex situ XRD patterns for the NiS_2 positive electrodes before electrochemical tests and at different states of discharge or charge during cycling. Notations A–G correspond to those in Fig. 4.



Figure 6. Ni K-edge XANES spectra for the NiS_2 positive electrodes before electrochemical tests and after the initial discharge (B in Fig. 4) and charge (E). Ni foil was used as a reference.

NiS₂ was fully utilized, which is consistent with the result that the first discharge capacity was close to the theoretical value. At this state, any other phases, such as Li₂S and Ni, which were anticipated to appear assuming an ideal electrochemical reaction (NiS₂ + 4Li \rightarrow Ni + 2Li₂S), were not obviously detected. These results indicate that the initial NiS₂ was deformed to an amorphous (or low crystallinity) phase by the Li insertion. At the end of the first charge (E), several small peaks, which were not assignable to any known phases, appeared. Although some small and broad peaks denoted by asterisks seemed to be located at close positions to those of NiS₂, which might suggest the partial recovering to NiS₂ after charging, detailed structural changes will be discussed later based on the results of extended XAFS (EXAFS). In the second cycle, the XRD patterns after discharge and charge (F and G) were very similar to those of the preceding discharged and charged states (B and E), respectively. Therefore, the present electrochemical redox reaction seemed to take place between two kinds of different deformed (or low-crystallinity) phases.

More detailed structural changes were examined by XAFS measurements. Figure 6 shows the ex situ Ni K-edge X-ray absorption near-edge spectroscopy (XANES) spectra for the initial positive electrode and those after the first discharge (B in Fig. 4) and charge (E). The spectrum of Ni foil is also shown for comparison. The edge position of the initial NiS2 electrodes shifted to lower energies after the first discharge (B), and returned to higher energies with the subsequent charging (E). This indicates that the average oxidation of Ni was lowered with the Li insertion and raised again with the subsequent Li extraction. A notable point is that the spectrum of the recharged sample did not completely overlap with that of the initial NiS₂ electrode, and its edge position was located between those of the initial and the discharged NiS_2 . This indicates that the NiS_2 , once fully reduced, was not completely reformed upon reoxidation, and some amounts of Ni with lower oxidation state (< +2) were present in the recharged samples.

The k^3 -weighted EXAFS oscillations and the corresponding magnitude of the Fourier transforms are shown in Fig. 7a and b. The initial NiS₂ electrodes showed a relatively sharp peak around 2 Å and a rather distinct long-range structure up to, at least, 4 Å. The discharged and charged samples showed a broad and complicated peak profile around 2 Å and rather indefinite structure beyond it, suggesting that these samples consisted of deformed structures



Figure 7. (a) k^3 -weighted EXAFS oscillations and (b) their Fourier transform magnitudes for the NiS₂ positive electrodes before electrochemical tests and after the initial discharge (B in Fig. 4) and charge (E). Corresponding spectra for Ni foil are also shown for comparison.

and/or several components. In order to clarify the structural environment around the absorbing Ni atoms, the curve-fitting analysis in *R*-space using theoretical phase shifts and backscattering amplitudes calculated by $\text{FEFF}^{21,22}$ was carried out based on the crystallographic data of the known compounds, such as Ni and NiS₂, ^{19,23} and

Table I. Interatomic distances (*r*) and Debye–Waller factors (σ^2) for the NiS₂ positive electrodes before electrochemical tests and after the initial discharge (B in Fig. 4) and charge (E). Crystallographic data estimated from the literature^{19,23} are also listed for comparison.

Sample	Shell	<i>r</i> (Å)	$\sigma^2~({\rm \AA}^2)$
Before electrocher	nical test		
	Ni–S	2.39	0.0098
	Ni–Ni	4.11	0.0169
After 1d (B)			
	Ni–S	2.17	0.0190
	Ni–Ni	2.53	0.0086
	Ni–Ni	3.76	0.0081
After 1c (E)			
	Ni–S	2.15	0.0161
	Ni–Ni	2.44	0.0114
	Ni–Ni	3.71	0.0076
Crystallographic d Ni metal ^a	ata		
	Ni–Ni	2.492	
NiS ₂ ^b			
2	Ni–S	2.396	
	Ni–Ni	4.014	
^a Ref. 23			
^b Ref. 19			

the results are listed in Table I. The Ni-S and Ni-Ni distances of the initial NiS₂ positive electrodes, which were consistent with those estimated from the previously reported crystallographic data, shortened after the discharge. This would be originated from some rearrangements of Ni and S ions by the Li insertion [probably including some disproportionation reactions, as indicated by the shift of the edge position in the XANES spectra (Fig. 6)], though its crystallographic structure cannot be definitely determined. The value of the Debye–Waller factor, which is the measure of random disor-der from the ideal atomic positions,²⁴ became larger for the Ni–S distance after the discharge. This indicates an increase in static disorder by the Li insertion and is consistent with the above-mentioned rearrangements of Ni and S ions. In addition, a shorter Ni-Ni distance (2.53 Å), which was close to that (2.492 Å) of the metallic Ni, was proposed by the fitting. This suggests that some amounts of metallic Ni would be present in the discharged NiS₂, though they were not detected in the XRD measurements (Fig. 5) probably due to fine particles and/or an amorphous phase. Thus, the Li insertion into the NiS₂ might give rise to rearrangements of Ni and S ions, resulting in the formation of deformed structures with shortened Ni-S and Ni-Ni distances, as well as the formation of small-sized metallic Ni clusters. Such structural environment remained nearly unchanged after the subsequent charging (Table I), though the average oxidation of Ni somewhat increased (Fig. 6), probably with changing the population of Ni-S pairs against Ni-Ni pairs. This suggests that the Ni-S distances, once shortened by the Li insertion, did not return to the initial value and the small-sized metallic Ni clusters still remained after the subsequent Li extraction. Therefore, several small peaks denoted by asterisks in Fig. 5 could not be assigned to NiS₂. Judging from the capacity values (Fig. 4), some amounts of Li seemed to still remain in the charged NiS₂ electrodes. Although the reason is not clear, such irreversibility of Li extraction from the deformed NiS₂ would explain the poor cyclability of the cells.

The electrochemical performances of FeS₂, which has the same type (pyrite) crystallographic structure to NiS₂, have been considerably studied and reported up to date.²⁴⁻²⁹ At lower current rates or at $>37^{\circ}$ C, a two-step reaction (FeS₂ + 2Li \rightarrow Li₂FeS₂ and Li₂FeS₂ + 2Li \rightarrow Fe + 2Li₂S) is observed during the first discharging to 1.0 V in the Li/FeS₂ cells with nonaqueous electrolytes, and each

Table II. Ratios of sulfur to fluorine contents (S/F) in the electrolytes measured by ion chromatography for the initial cells and those after the first discharge (B in Fig. 4) and the charge (E).

Sample	S/F (mol %)
Before electrochemical test	0.01(1)
After 1d (B)	0.02(1)
After 1c (E)	0.02(1)

reaction gives rise to a plateau in the discharge curve. The intermediate phase Li₂FeS₂ is not detected by XRD, because such a phase, formed electrochemically around room temperature, is apparently amorphous.^{25,26} In the subsequent charging to 2.8 V, the reverse reaction proceeds to form first the intermediate phase Li₂FeS₂, but finally the positive electrode becomes a mixture of FeS_v and S, not FeS₂, which explains why the Li/FeS₂ cells show poor reversibility.^{25,26} Similar electrochemical reactions might proceed in the present Li/NiS₂ cells. The initial NiS₂ might be changed to an amorphous Li_xNiS₂ phase by the Li insertion, which was not detected by the XRD measurements as in the case of Li₂FeS₂. At the end of discharging, it might result in the formation of deformed structures with shortened Ni-S and Ni-Ni distances, as well as the formation of small-sized metallic Ni clusters, as discussed above. In the subsequent charging, the Li extraction proceeded to form another deformed structure with some amounts of Li ions remaining, but not to finally form the initial NiS₂ at the end of it. Because the formation of the initial NiS2 does not occur, the second discharge showed different profile from the first discharge (Fig. 4), and such irreversibility of the Li extraction from the deformed, lithiated structure would explain the poor cyclability of the cells.

Besides the above irreversibility, there have been other factors reported for the poor cyclability of the Li/FeS2 cells: (i) the formation of polysulfides during charging (at >2.25 V), which were soluble in nonaqueous electrolytes: (ii) the partial loss of the electrical contact among the cathode active materials and current collector; and (iii) the formation of iron sulfates at the surface of (particularly freshly cleaved) FeS₂ by exposing to oxygen and/or moisture, which could form a barrier for migration of Li⁺ into the underlying pyrite lattice, as well as degrade the electrolytes during the electro-chemical tests.^{1,6,24,29,30} Similar degradation mechanisms would proceed in the present Li/NiS_2 cells. We first examined the sulfur contents in the $LiPF_6/(EC + DMC)$ electrolytes after the initial discharge and charge, and the results are listed in Table II. Although the measured values were close to the lower detection limit, they were nearly unchanged after the initial discharge and charge. Particularly, the value after 1c was much less than that (S/F = 0.14)anticipated from the capacity loss (ca. 290 mAh g⁻¹, Fig. 4) assuming that it was entirely due to the dissolution of sulfur from the positive electrodes. Therefore, the formation of soluble polysulfides would not be a dominant factor for the poor cyclability in the present Li/NiS₂ cells. This is also suggested by the morphological changes of the NiS₂ electrodes, as shown in Fig. 8. After the elec-



Figure 8. SEM images for the NiS₂ positive electrodes (a) before and (b) after the electrochemical tests over 10 cycles at 175 mA g^{-1} (0.2 C). Magnification is the same for each photograph.



Figure 9. Cycle performances for the nonground and ground $\rm NiS_2$ sample cells at 175 mA g^{-1} (0.2 C).

trochemical tests over 10 cycles, any humps, which were formed when sulfur-based active materials were dissolved into electrolytes, were not observed. Instead, we observed several cracks on the surface of the electrodes (Fig. 8b), indicating electrical disconnections among the active materials, carbon powders, and/or current collectors, which might be generated by the volumetric changes of the active materials during the electrochemical redox cycling. For suppressing such volumetric changes, we ground the present NiS₂ powder by a mechanical milling process and the cycle performance was examined. The ground powder consisted of submicrometer-sized primary particles (Fig. 2d), and its XRD pattern showed broad peaks, assigned to NiS₂, without any impurity phases (Fig. 3c). The discharge capacity of the ground NiS₂ sample cells showed lower values and rapid degradation with cycling; the capacity retention at the 10th cycle was much reduced (ca. 10%) as compared to that of the nonground sample cells (ca. 19%), as shown in Fig. 9. This inferior cyclability would be mainly originated from some surface impurities (not detectable by XRD), such as absorbed water and/or nickel sulfates, formed by reacting the activated NiS₂ surface with oxygen and/or moisture, which might impede the Li⁺ migration into the underlying NiS₂ lattices as well as directly degrade the electrolytes. Therefore, for obtaining better cyclability in the Li/NiS₂ cells, suppressing the formation of surface impurities, as well as improving the reversibility of Li extraction from the lithiated (discharged) NiS₂ and minimizing the volumetric changes of the active materials, seems necessary, and modifications of NiS₂ for such approaches are now underway.

Conclusions

We have successfully prepared porous NiS₂ (porosity 89%), containing trace amounts (ca. 3%) of NiS, and finally single-phase NiS₂

powder by the SPS treatment of the sponge-shaped porous Ni (porosity 95%) and sulfur powder. The obtained single-phase NiS₂ sample cells showed the initial discharge capacity of ca. 820 mAh g⁻¹, which was \sim 94% of the theoretical value. The capacity retention after 10 cycles was ca. 19%, and such rapid degradation was mainly attributable to the irreversibility of the Li extraction from the lithiated (discharged) NiS2 electrodes and the electrical disconnections among the active materials, carbon powders, and/or current collectors.

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