Lithium-sulfur cells using sulfur as an active cathode material offer high energy density and low-cost. However, dissolution and migration of lithium polysulfides (the ‘shuttle effect’) remain key obstacles for the practical development of lithium-sulfur cells. Here, we demonstrate that Fe$_{1-x}$S (pyrrhotite) coated by N-doped carbon (Fe$_{1-x}$S@NC) with high affinity for polysulfides and high electronic conductivity can be used as a functional additive to trap lithium polysulfides and reutilize reaction intermediates in the sulfur cathode during cycling. The addition of Fe$_{1-x}$S@NC into the sulfur cathode results in the enhancement of cycling performance of the lithium-sulfur cell in terms of initial discharge capacity, capacity retention and rate capability. This superior cycling performance can be attributed to strong chemical interactions between electrically conductive Fe$_{1-x}$S@NC particles and lithium polysulfides, which suppress the dissolution of lithium polysulfides and enhance the utilization of active sulfur during repeated cycling.

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kept at 500 °C for 5 h under an argon atmosphere to induce both sulfurization of Fe2O3 and carbonization of PDA. The same procedure was followed to prepare Fe1−xS by direct sulfurization of Fe2O3 with thioacetamide.

Electrode preparation and cell assembly.—Sulfur powder (Sigma-Aldrich), Fe1−xS@NC, Super-P carbon (MMM co.) and poly(vinylidene fluoride) (PVdF, Solfel 5130, Solvay) binder were dispersed in N-methyl pyrrolidinone (NMP, Sigma-Aldrich) at a mass ratio of 60/15/15/10 to prepare the viscous slurry for sulfur cathode. For comparison, the same amount of Fe2O3@NC was substituted with Fe2O3 and Super-P for making sulfur-Fe2O3 and sulfur only electrode, respectively. The content of electrode components in different types of cathodes is given in Table I. The obtained slurry was coated onto carbon-coated aluminum foil using a doctor blade followed to prepare Fe1−xS by direct sulfurization of Fe2O3 with thioacetamide.

Results and Discussion

Figure 1a presents the TEM image of synthesized Fe1−xS@NC particles, showing an irregular spherical shape with an average particle size less than 1 μm. A magnified image of a single Fe1−xS@NC particle is given in Figure 1b, illustrating a core-shell structure with N-doped carbon coated on the surface of the Fe1−xS core particle. Here, the N-doped carbon coating layer on Fe1−xS was formed by the polymerization of dopamine, followed by carbonization under an inert atmosphere. The thickness of the coating layer was measured to be about 27 nm. No distinct lattice fringe patterns could be observed in the coating layer on the Fe1−xS@NC particle (Figure 1c), indicating an amorphous nature of the N-doped carbon.45 Lattice fringe patterns of Fe1−xS core particles could be identified and the corresponding lattice spacing was about 0.45 nm. The SAED pattern in Figure 1d shows the N-doped carbon layer with diminished bright Fe1−xS rings. This confirms that Fe1−xS@NC has a polycrystalline nature with imperceptible rings. Figures 2b–2f show element mappings of an Fe1−xS@NC particle with its TEM image (Figure 2a); these confirm that all elements (i.e., Fe, S, C, and N) are uniformly distributed in the Fe1−xS@NC particle. These results indicate the successful synthesis of core-shell structured Fe1−xS@NC particles consisting of a polycrystalline Fe1−xS core and amorphous N-doped carbon-coating layer. The crystalline structures of the prepared materials were characterized by X-ray diffraction (XRD) analysis. Figure 3a shows the XRD patterns of the Fe2O3, Fe1−xS, and Fe1−xS@NC particles. The XRD pattern of the Fe2O3 particles presents well-defined crystalline peaks at 2θ = 31.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°, 62.4°, and 64.0°, corresponding to the orthorhombic crystal structure; all the diffraction peaks were well matched with JCPDS card no: 89-2810. The diffraction peaks observed in the Fe1−xS and Fe1−xS@NC particles could be unambiguously assigned to the hexagonal phase of Fe1−xS without any impurity peaks or other phases, indicating that Fe2O3 particles were converted to Fe1−xS phase during sulfurization. The crystalline peaks observed at 2θ = 29.9°, 33.8°, 43.8°, 53.1°, 57.4°, 65.2°, 71.2° and 74.2° can be assigned to the (100), (101), (102), (110), (103), (201), (202), and (104) planes, respectively.42 As shown in figure, the hexagonal phase of the Fe1−xS core in the Fe1−xS@NC was well maintained even after carbonization at high temperature. No crystalline peaks for N-doped carbon could be observed in the XRD pattern of Fe1−xS@NC, which reveals that the amorphous N-doped carbon was coated on the surface of the pyrrhotite Fe1−xS core particle. To further examine the chemical nature of the Fe1−xS@NC particle, XPS analysis was performed. In Fe2p core-level spectrum (Figure 3b), two major peaks were observed at 710.8 and 724.5 eV, which are attributed to the Fe2p3/2 and Fe2p1/2, respectively.43 The broad peaks at 163.6 and 164.8 eV in Figure 3c can be attributed to S2p1/2 and S2p3/2, respectively.44 The presence of oxidized groups (SOx) was identified at the high binding energy, C1s core-level spectrum in Figure 3d can be resolved into 284.7, 285.8 and 288.5 eV, which correspond to the C−C, C−N, C−O bonds, respectively. The N1s core-level spectrum shown in Figure 3e can be deconvoluted into three major peaks at the binding energies of 397.5, 399.5 and 400.5 eV, which are attributed to the pyridinic-N, pyrrolic-N and graphic-N bonds, respectively.45 To estimate the amount of carbon present in the Fe1−xS@NC particle, TGA was performed and the result is presented in Figure 3f. The initial weight gain was caused by the partial conversion of Fe1−xSi into Fe2O3, as previously reported.46 The final weight loss can be ascribed to the decomposition of unreacted Fe1−xS and FeSO4 into Fe2O3 and the decomposition of carbon into CO2. From the TGA analysis, the amount of carbon present in the Fe1−xS@NC particle was calculated to be 15.2%.

Poly sulfide adsorption ability is one of the most important factors when choosing an appropriate material for chemical confinement of soluble lithium polysulfides formed in the sulfur cathode. To investigate the polysulfide adsorption ability of various materials, Li2S4 was chosen as a model polysulfide because it is the most commonly used in current technology.
produced among the soluble lithium polysulfides ($\text{Li}_2\text{S}_x$, $4 \leq x \leq 8$) when sulfur is fully reduced to $\text{Li}_2\text{S}$ during the discharge process. Another reason for choosing $\text{Li}_2\text{S}_x$ as a model polysulfide was that $\text{Li}_2\text{S}_x$ remains the longest in the electrolyte solution and its migration to the anode side would be the most probable among the soluble lithium polysulfides, since the reduction of $\text{Li}_2\text{S}_x$ into $\text{Li}_2\text{S}$ is obviously the most sluggish step except for the solid-solid reaction of $\text{Li}_2\text{S}_x$ to $\text{Li}_2\text{S}$ during the discharge process. To compare the polysulfide adsorption abilities of various materials, the color changes of $\text{Li}_2\text{S}_4$ solutions containing MWCNT, Super-P, $\text{Fe}_2\text{O}_3$ and $\text{Fe}_{1-x}\text{S}@\text{NC}$ were monitored using a digital camera as a function of time. It should be noted that the amount of materials added into the vials of polysulfide solution are same (60 mg each). As shown in Figure 4, four types of test materials were floating in the $\text{Li}_2\text{S}_4$ solution and there was little color change in the solution after 0.1 h. However, we could clearly observe the difference in the color of the $\text{Li}_2\text{S}_4$ solutions after 6.0 h. When adding $\text{Fe}_{1-x}\text{S}@\text{NC}$ into the $\text{Li}_2\text{S}_4$ solution, the color of the solution turned from yellow to colorless, indicating that most of $\text{Li}_2\text{S}_4$ in the solution was trapped by the $\text{Fe}_{1-x}\text{S}@\text{NC}$ owing to strong interaction between $\text{Fe}_{1-x}\text{S}@\text{NC}$ particles and $\text{Li}_2\text{S}_4$. On the other hand, the $\text{Li}_2\text{S}_4$ solution containing $\text{Fe}_2\text{O}_3$ remained light yellowish in color, implying a deficient ability of $\text{Fe}_2\text{O}_3$ to trap lithium polysulfides as compared with $\text{Fe}_{1-x}\text{S}@\text{NC}$. In contrast, the color of the $\text{Li}_2\text{S}_4$ solutions containing MWCNT and Super-P remained intact (yellow) after 6.0 h, which suggests that these carbonaceous materials could not adsorb the $\text{Li}_2\text{S}_4$ in the solution. BET surface area of $\text{Fe}_{1-x}\text{S}@\text{NC}$ was measured to be 4.8 m$^2$ g$^{-1}$, which is much lower than those of MWCNT and Super-P carbon. These results demonstrate that the adsorption ability of $\text{Fe}_{1-x}\text{S}@\text{NC}$ is much higher than that of carbonaceous materials, even though it has a smaller surface area than MWCNT and Super-P carbon. The superior adsorption ability of $\text{Fe}_{1-x}\text{S}@\text{NC}$ for lithium polysulfides arises from the Lewis acid-base interactions between $\text{Fe}_{1-x}\text{S}@\text{NC}$ particles and polysulfides.

Electronic conductivity of an additive material for trapping lithium polysulfides is another crucial property in additives for chemical confinement, since the lithium polysulfides trapped by the additive must be reutilized during subsequent cycles. In this regard, the electronic conductivity of $\text{Fe}_{1-x}\text{S}@\text{NC}$ and $\text{Fe}_2\text{O}_3$ should be measured and compared. However, their intrinsic electronic conductivity could not be measured directly, because pelletizing using these particles was not possible owing to their brittle nature. Instead, $\text{Fe}_{1-x}\text{S}@\text{NC}$ or $\text{Fe}_2\text{O}_3$ was mixed with $\text{KBr}$ in same weight ratio (1:3) to prepare the solid-state pellet for conductivity measurements. As a result, the pellet prepared with $\text{Fe}_{1-x}\text{S}@\text{NC}$ particles showed considerably higher electronic conductivity (0.30 S cm$^{-1}$) than the $\text{Fe}_2\text{O}_3$-based pellet (0.01 S cm$^{-1}$), indicating the higher electronic conductivity of $\text{Fe}_{1-x}\text{S}@\text{NC}$ as compared with $\text{Fe}_2\text{O}_3$ particles. It should be noted that the electronic conductivity of $\text{Fe}_{1-x}\text{S}@\text{NC}$ must be significantly...
higher than the measured value (0.30 S cm$^{-1}$), since the pellet for the conductivity measurement contained high amounts (75 wt%) of KBr, which is electronically non-conductive. According to a previous study,$^{47}$ the electronic conductivity of Fe$_{1-x}$S is in the range of 200 to 1,000 S cm$^{-1}$. It has been reported that the electronic conductivity of 10$^{-1}$ S cm$^{-1}$ is enough for materials to be used as cathode active materials.$^{48}$ Figure 5 shows the SEM image of the sulfur cathode containing Fe$_{1-x}$S@NC particles and corresponding EDS elemental mapping images. The sulfur electrode is uniform and highly porous, both of which are necessary for good accessibility of liquid electrolyte into the electrode and good accommodation of large volume change during repeated cycles. Elemental mapping images of S, Fe and N in Figures 5b–5d demonstrate that Fe$_{1-x}$S@NC particles were mixed well with active sulfur material and were uniformly distributed throughout the sulfur cathode.

The cycling performance of the Li-sulfur cells assembled with different cathodes was evaluated in the voltage range of 1.8 to 2.6 V at a constant current rate of 0.2 C, and the resulting charge-discharge voltage profiles are given in Figures 6a–6c. The voltage profiles exhibit two discharge plateaus and a long charge plateau. The discharge plateaus at around 2.35 and 2.10 V correspond to the reduction of elemental sulfur to higher order lithium polysulfides (Li$_2$S$_x$, 4 ≤ x ≤ 8) that are soluble in the electrolyte and the reduction of long-chain polysulfides to insoluble Li$_2$S, respectively. The long charge plateau arises from the oxidation of Li$_2$S to cyclic sulfur. It can be clearly seen that the capacity delivered during lower discharge plateau was the highest in the Li-sulfur cell with Fe$_{1-x}$S@NC. This result suggests that most of the soluble lithium polysulfides formed in the sulfur cathode are trapped by Fe$_{1-x}$S@NC particles and reutilized for the subsequent reaction to produce Li$_2$S from the trapped lithium polysulfides during the lower discharge plateau period. While the cells with Fe$_2$O$_3$ and Fe$_{1-x}$S@NC exhibited similar capacity during the higher discharge plateau, there was a large difference in discharge capacity during the lower discharge plateau. Moreover, the second discharge plateau observed in the cell with Fe$_2$O$_3$ was not flat, implying unstable formation of Li$_2$S from the lithium polysulfides due to the electronically insulating nature of Fe$_2$O$_3$. As a result, the Li-sulfur cell with Fe$_{1-x}$S@NC delivered the higher initial discharge capacity (999.0 mAh g$^{-1}$) based on the mass of only sulfur material in the cathode. It should be noted that the reversible capacity of Fe$_{1-x}$S@NC material is very low in the voltage range of 1.8 to 2.6 V, and thus the contribution of the Fe$_{1-x}$S@NC to the specific capacity of the sulfur electrode is negligible. As shown in figures, the initial discharge capacity of the cell without any additives was the lowest (694.8 mAh g$^{-1}$), indicating that large amount of lithium polysulfides were dissolved into the electrolyte solution and migrated to the anode side. Cycling
Figure 3. (a) XRD patterns of Fe$_2$O$_3$, Fe$_{1-x}$S and Fe$_{1-x}$S@NC particles. XPS spectra of the (b) Fe2p core-level, (c) S2p core-level, (d) C1s core-level and (e) N1s core-level of Fe$_{1-x}$S@NC. (f) TGA curve of the Fe$_{1-x}$S@NC material.

performance of the Li-sulfur cells with different electrodes is compared in Figure 6d. The Li-sulfur cell without any additives showed a large capacity fading with cycling, which can be attributed to the gradual loss of active sulfur from the sulfur cathode. Although the Li-sulfur cell with Fe$_2$O$_3$ exhibited higher discharge capacity and better cycling stability as compared with the cell without additive, its capacity retention was inferior to the cell with Fe$_{1-x}$S@NC. The Li-sulfur cell with Fe$_{1-x}$S@NC delivered high discharge capacities throughout cycling and exhibited the best capacity retention (74.8% of its initial capacity) among the cells after 300 cycles. In addition, the cell with Fe$_{1-x}$S@NC showed the higher coulombic efficiency than any other cells during cycling. As discussed, most of the lithium polysulfides can be trapped in the sulfur cathode containing Fe$_{1-x}$S@NC; they can then be reutilized in subsequent cycles, which results in stable cycling and high coulombic efficiency.

To understand the cycling behavior of cells with different sulfur cathodes, AC impedance measurements of the cells were conducted after the 1st and 300th cycles. As shown in Figure 7, all cells showed two overlapping semicircles with a real axis intercept. The X-axis intercept observed at the highest frequency corresponds to the electrolyte resistance, the first semicircle in the high frequency range can be ascribed to Li$^+$ ion migration through the surface film on the electrode, and the second semicircle in the middle to low-frequency range is related with charge transfer reaction at the electrode-electrolyte interface. The three different resistances were designated as electrolyte resistance ($R_e$), film resistance ($R_f$) and charge transfer resistance ($R_{ct}$). When the first cycle was finished, all three cells exhibited similar resistances. However, the electrolyte resistances were found to increase after cycling. An increase in electrolyte resistance in the Li-sulfur cell can mainly be ascribed to the increase in viscosity of electrolyte solution due to gradual dissolution of lithium polysulfides into the electrolyte from the sulfur cathode during cycling. It is noticeable that cells without additives showed a drastic increase in electrolyte resistance, whereas the cell with Fe$_{1-x}$S@NC exhibited a small increase in electrolyte resistance. This result suggests that a lower amount of lithium polysulfides are dissolved into the electrolyte in cells with Fe$_{1-x}$S@NC, because Fe$_{1-x}$S@NC particles can effectively trap lithium polysulfides within the sulfur cathode. The
interfacial resistances in cell without additives were also significantly increased after 300 cycles. This is because the dissolution and migration of polysulfides to the anode side causes the degradation of interfacial contacts in the sulfur cathode and the retardation of the charge transfer reaction at the electrode-electrolyte interface. In addition, the migrated lithium polysulfides could be deposited on the surface of the lithium anode, resulting in an increase of surface film resistance. In contrast, the cell with Fe$_{1-x}$S@NC showed a relatively small increase in interfacial resistances after 300 cycles, resulting in the lowest cell resistance among the cells investigated. These results demonstrate that the addition of Fe$_{1-x}$S@NC with good adsorption ability for polysulfides and high electronic conductivity effectively traps and reutilizes lithium polysulfides within the cathode side, resulting in superior cycling performance as compared with the other two cells.

The rate capability of the Li-sulfur cell with different sulfur cathodes was evaluated at various C rates. In the rate capability test, the cells were charged and discharged at different current rates with increasing current rate from 0.1 to 5.0 C every five cycles. Figure 8a shows the charge and discharge curves of the Li-sulfur cell with Fe$_{1-x}$S@NC at different C rates, plotted for the first cycle at each C rate. With increasing current rate, the overpotential increased and the discharge capacity was decreased with shortening discharge plateaus. From the cycling of cells with different cathodes at various current rates, their rate performance is compared (Figure 8b). Clearly, the Li-sulfur cell with Fe$_{1-x}$S@NC delivered the highest discharge capacities at all C rates. The enhanced high-rate performance can be attributed to suppression of polysulfide dissolution due to effective trapping by Fe$_{1-x}$S@NC and enhanced electronic conductivity. Although Fe$_2$O$_3$ particles have a little ability to adsorb lithium polysulfides, as demonstrated in Figure 4, their insulating nature significantly reduces the discharge capacity at lower discharge plateaus at high current rates. As a result, the discharge capacity of the cell with Fe$_2$O$_3$ was dropped from 938.4 to 84.9 mAh g$^{-1}$ when the current rate was increased from 0.1 to 5.0 C. The Li-sulfur cell with Fe$_{1-x}$S@NC recovered its discharge capacity when the C rate was decreased from 5.0 to 0.1 C. These results suggest that the addition of Fe$_{1-x}$S@NC into the sulfur cathode not only increases cycling stability but also improves the rate capability of Li-sulfur cells.

**Conclusions**

Fe$_{1-x}$S uniformly coated by N-doped carbon (Fe$_{1-x}$S@NC) was synthesized and used as an additive for chemical confinement of lithium polysulfides in Li-sulfur cells. The addition of Fe$_{1-x}$S@NC into the sulfur cathode not only suppressed the migration of lithium...
Figure 5. (a) SEM image of the sulfur electrode containing Fe$_{1-x}$S@NC particles and its EDS elemental mappings corresponding to (b) S, (c) Fe and (d) N.

Figure 6. Charge and discharge voltage profiles of the Li-sulfur cells assembled with different sulfur cathodes at constant current rate of 0.2 C. (a) Sulfur without additives, (b) sulfur with Fe$_2$O$_3$ and (c) sulfur with Fe$_{1-x}$S@NC. (d) Discharge capacities and coulombic efficiencies of the Li-sulfur cells with different sulfur cathodes at 0.2 C rate as a function of cycle number.
polysulfides toward lithium anode by effectively trapping polysulfides but also enhanced the electronic conductivity for reutilization of trapped lithium polysulfides within the sulfur cathode. As a result, the Li-sulfur cell with Fe$_{1-x}$S@NC delivered a high initial discharge capacity of 999.0 mAh g$^{-1}$ with good capacity retention and exhibited an enhanced rate capability. Further tailoring the morphology of such additive materials would provide a more beneficial effect on the cycling performance of Li-sulfur cells.

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ORCID

Dong-Won Kim https://orcid.org/0000-0002-1735-0272

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