Manipulating local environment of atomically dispersed Fe electrocatalyst for high energy and long cycle Li-S pouch cell

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Abstract

High-energy lithium-sulfur (Li-S) pouch cell are limited by the insufficient capacities and stabilities of their cathodes under practical electrolyte/sulfur (E/S), electrolyte/capacity (E/C), and negative/positive (N/P) ratios. Herein, we fabricated an advanced cathode comprising highly active Fe single atom catalysts (SACs) and porous carbon to attain 361.8 W h kg⁻¹ Li-S pouch cells satisfying low E/S (2.0), E/C (1.9), and N/P (2.3) ratios with high sulfur loadings (8.4 mg cm⁻²). We designed high-activity Fe SACs by manipulating their local environments using electron exchangeable binding (EEB) sites. Introducing EEB sites composed of two different types of S species, namely, thiophene-like-S and oxidized-S, adjacent to Fe SACs, promoted the kinetics of the Li₂S redox reaction by providing additional binding sites and modulating the Fe *d*-orbital levels via electron exchange with Fe. This desirable cathode electrocatalysis is maximized by the intimate contact of Fe SACs with the S species, confined together into porous carbon.

Introduction

Lithium-sulfur (Li-S) batteries are attracting world-wide attention owing to their high theoretical gravimetric energy density (W_G) values, which are required to attain 400-600 W h kg⁻¹ pouch cells to practically compete with commercial lithium ion batteries (LIBs, 250-300 W h kg⁻¹).^{1,2} However, the lithium polysulfide (LiPS) shuttling phenomenon and sluggish reaction kinetics in the cathode limit the W_G of a Li-S battery.³⁻⁶ Although the pioneering Li-S battery corporations (Sion Power and Oxis Energy) developed 400-450 W h kg⁻¹ prototype with advanced pouch cell manufacturing technology, most Li-S pouch cells in academic research still exhibit similar levels of W_G compared to LIBs, despite significant improvements on the coin-cell level.⁷⁻¹⁰ It is because high-performance coin-cell was achieved under flooded electrolyte, excess Li (> 500%), and low S loading (< 4 mg cm⁻²) conditions, which were favorable for a high capacity and cycle stability but led to “fat” Li-S cells.¹¹⁻¹⁴ To develop “light” Li-S pouch cells with high energies, a rational cathode design is needed with sufficiently low electrolyte/sulfur (E/S < 5 μ L mg⁻¹), electrolyte/capacity (E/C < 5 μ L [mA h]⁻¹), and negative/positive capacity (N/P < 5) ratios, and a high S loading (> 5 mg cm⁻²), to minimize the amount of excess Li and electrolyte.^{12,15-17}

Electrocatalysis is at the forefront of Li-S cathode design technology because the multi-functional electrocatalysts based on the adsorption/conversion behaviors of S species allow the cathode to exhibit a high capacity and stable cycle even under a high S loading, with low E/S and N/P ratios (Supplementary Fig. 1).¹⁸⁻²² In particular, single atom catalysts (SACs) are the most promising owing to their following exceptional characteristics (Supplementary Fig. 2a): i) SACs exhibit high atom utilization efficiencies, so minimizing catalyst contents in the electrode, and offers the opportunity to deliver high-energy pouch cells,^{23,24} ii) SACs allow the direct conversion of adsorbed LiPS to the final products without an additional sluggish diffusion step. The superior qualities of SACs motivate efforts toward developing SAC-embedded cathodes for high-energy Li-S cells.²⁵⁻²⁷ However, they are disrupted by the

intrinsic limitations of SACs, including unsatisfactory catalytic activities and weak adsorption strength with S species (due to the Lewis acid-base interaction with single-end binding).^{28,29} Consequently, metal compound (M_aX_b , M=metal and X=anion) based particle-type catalysts (PTCs) are used together with SACs in the cathode, owing to their strong adsorption abilities with LiPS by forming M-S and X-Li bonds.^{25,30} However, PTCs decrease the atom utilization efficiency, which necessitates a high catalyst content (10-30 wt%) in the cathode,^{31,32} restricting the W_G values of the Li-S pouch cells (Supplementary Fig. 2b). Moreover, an additional LiPS diffusion step is inevitable because of the low electrical conductivities of most PTCs.³³ Consequently, state-of-the-art SAC-based cathodes exhibit unsatisfactory pouch cell performances ($< 300 \text{ W h kg}^{-1}$, considering all pouch cell components) and cycle life (< 70 cycles) (Supplementary Fig. 3). In this regard, strategies to enhance the sulfur adsorption properties and catalytic activities of SACs are required for the fabrication of Li-S pouch cells with a higher W_G than the currently known cells.

Herein, we propose a concept for designing highly active Fe-N-C catalysts by manipulating their local environment using electron exchangeable binding (EEB) sites for achieving high-energy Li-S pouch cells (Fig. 1a). EEB sites adjacent to the Fe-N-C catalysts provide additional binding sites for the S species and modulate the Fe d -orbital energy level via electron exchange with the Fe atom. These multi-functional EEB sites enhance the LiPS adsorption properties and Li_2S redox kinetics, leading to highly active Fe SACs that are distinctly different from conventional SACs. Especially, the mesoporous carbon host holds the Fe SACs, electrolytes, and S species together, stably retaining the triple-phase boundaries for Li^+ ion-catalysts-electron (Fig. 1b). This specially designed cathode with desirable Li-S electrochemistry enables high energy ($325.4 \text{ W h kg}^{-1}$) Li-S pouch cells with stable cycle life up to 80 cycles. We also successfully fabricated a $361.8 \text{ W h kg}^{-1}$ Li-S pouch cell satisfying low E/S ($2.0 \mu\text{L mg}^{-1}$), E/C ($1.9 \mu\text{L [mA h]}^{-1}$), and N/P (2.3) ratios with a high S loadings of 8.4 mg cm^{-2} .

Main Text

Manipulation of the local environment of Fe SACs with EEB sites

Based on the biological phenomenon where the redox catalysis of cytochrome is altered by the oxygen binding properties of different functional groups around the Fe-N-C sites (Supplementary Fig. 4), we designed highly active Fe-N-C catalysts in mesoporous carbon by manipulating their local environments using EEB sites comprising two different S species: thiophene-like-S (-S) and oxidized-S ($-\text{SO}_2$) (Fig. 2a). Two different precursors: dibenzyl disulfide (DBDS) and sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) were used to modulate the atomic ratios of the -S and $-\text{SO}_2$ species for the design of highly optimized EEB sites. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-prepared mesoporous carbon clearly show well-developed porous architectures (Supplementary Fig. 5a and b), consistent with the nitrogen physisorption results (Supplementary Fig. 6). Even after introducing Fe-N-C, the three different SACs, namely, Fe-N-C without EEB sites (FeNC), Fe-N-C with DBDS-derived EEB

sites (FeNC-EEB-1), and Fe-N-C with Na₂S₂O₅-derived EEB sites (FeNC-EEB-2), still showed mesopores (Supplementary Fig. 7), and the materials exhibited similar surface areas, pore sizes, and pore volumes (Supplementary Fig. 8 and Supplementary Table 1).

The local Fe-N-C environment was investigated using X-ray spectroscopy and electron microscopy techniques. First, X-ray photoelectron spectroscopy (XPS) S 2p spectra of FeNC-EEB-1 and FeNC-EEB-2 exhibit two characteristic peaks of -S at 163.7 and 164.9 eV corresponding to C-S-C 2p 3/2 and C-S-C 2p 1/2, respectively and one characteristic peak of -SO₂ at 168.0 eV (Fig. 2b and c), indicating that the EEB sites derived from DBDS and Na₂S₂O₅ are composed of -S and -SO₂ species.³⁴ However, the -SO₂/-S ratio of the EEB sites adjacent to Fe-N-C was highly dependent on different precursors (Fig. 2d). The FeNC-EEB-1 (0.12) exhibits a ~5 times lower -SO₂/-S ratio than FeNC-EEB-2 (0.63). This is because Na₂S₂O₅ is a more suitable precursor to form -SO₂ species at high temperatures owing to its higher atomic O fraction compared to DBDS.³⁵ Furthermore, Fe and N atomic contents are similar in all the materials (Fig. 2d, Supplementary Fig. 9 and 10). Second, the high-angle annular dark-field scanning transmission electron microscopy (STEM) image of FeNC shows atomically dispersed Fe in the carbon matrix (Supplementary Fig. 11a). These Fe single atoms were also observed in FeNC-EEB-1 and FeNC-EEB-2 (Fig. 2e and Supplementary Fig. 11b), indicating the existence of Fe SACs inside the porous carbon. Moreover, the energy dispersive spectroscopic (EDS) mapping images of FeNC-EEB-1 and FeNC-EEB-2 represent the homogeneous distributions of Fe, N, C, S, and O along the particles, implying the formation of Fe-N-C and EEB sites (Supplementary Fig. 12).

To study the chemical states of Fe-N-C, Fe K-edge X-ray absorption spectroscopy (XAS) was performed.³⁶ In the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectrum of the Fe foil, the Fe-Fe metallic bonding peak is observed at 2.2 Å (Fig. 2f).³⁷ However, this Fe-Fe peak disappeared and new peaks corresponding to Fe-N and Fe-C appeared at 1.4 and 2.4 Å,³⁷ respectively in the spectra of FeNC, FeNC-EEB-1, and FeNC-EEB-2, demonstrating the presence of Fe-N-C sites without Fe metallic particles. The X-ray diffraction (XRD) results also indicated the absence of other crystalline phases (*e.g.*, Fe metal and iron nitride) (Supplementary Fig. 13). Furthermore, the X-ray absorption near-edge structure (XANES) spectra showed that the white line intensity of FeNC-EEB-2 was higher than that of FeNC, whereas FeNC-EEB-1 exhibited a lower white line intensity than FeNC (Fig. 2g). FeNC-EEB-1 has a low -SO₂/-S ratio and exhibits an upshift of the Fe *d*-band center, implying that electrons transfer from the neighboring EEB sites to Fe. In contrast, FeNC-EEB-2 has a high -SO₂/-S ratio and shows a downshift of the Fe *d*-band center, indicating that electrons transfer from Fe to the EEB sites.³⁴ To verify the electron exchange between Fe and -SO₂/-S EEB sites, density functional theory (DFT) calculations were performed (Supplementary Fig. 14).³⁴ The -S species represent the electron donation to Fe-N-C, corresponding to an increase in the Fe *d*-orbital level, while the -SO₂ species show the electron withdrawal from Fe-N-C, indicating a decrease in the Fe *d*-orbital level. This is consistent with the tendency of observed in the XANES spectra, demonstrating that the introduction of EEB sites with different -SO₂/-S ratios near the Fe-N-C catalysts leads to the modulation of *d*-orbitals of Fe SACs by electron exchange.

Li₂S redox kinetics on Fe SACs

Effects of the local Fe-N-C environment, manipulated by EEB sites, on the Li-S electrochemistry were studied using a coin-cell. The cyclic voltammetry curve of FeNC-EEB-1 exhibits two cathodic peaks I and II at higher potentials than FeNC (Supplementary Fig. 15), indicating that the EEB sites with a low -SO₂/-S ratio near Fe-N-C decrease the reduction overpotential. However, FeNC-EEB-2 exhibits similar potentials of cathodic peaks I and II as those of FeNC, implying that the EEB sites with high -SO₂/-S ratios are not much effective in decreasing the reduction overpotential. In the oxidation reaction, both FeNC-EEB-1 and FeNC-EEB-2 exhibit the anodic peak III at a lower potential than FeNC, indicating that both EEB sites improve the oxidation overpotential. Tafel plots were obtained to further evaluate the sulfur redox kinetics (Fig. 3a). The Tafel slope of FeNC-EEB-1 was much lower than that of FeNC, while the Tafel slope of FeNC-EEB-2 was slightly lower than that of FeNC for the cathodic reaction. In the anodic reaction, both FeNC-EEB-1 and FeNC-EEB-2 exhibited lower Tafel slopes than FeNC, demonstrating that the -SO₂/-S EEB sites near the Fe-N-C catalysts improved the sulfur redox kinetics.

Potentiostatic analyses were performed to understand the enhanced kinetics of sulfur electrochemistry by EEB sites on the Li₂S nucleation/dissociation behaviors. During the potentiostatic discharge at 2.05 V, FeNC-EEB-1 exhibited the maximum current time (t_m) at 227 s, which was earlier than that of FeNC (Fig. 3b and Supplementary Fig. 16a). The FeNC-EEB-2 exhibited the t_m at 320 s, which was slightly earlier than FeNC but later than FeNC-EEB-1 (Supplementary Fig. 16b). Considering that the t_m is highly related to the Li₂S nucleation density (N_o) and growth rate (k^2) as follows,³⁸

$$t_m = (2\pi N_o k^2)^{-0.5}$$

the lowest t_m in FeNC-EEB-1 indicates that Li₂S nucleation is promoted by EEB sites with a low -SO₂/-S ratio. The enhanced Li₂S nucleation in FeNC-EEB-1 leads to a higher Li₂S nucleation capacity (213.3 mA h g⁻¹) than FeNC (185.3 mA h g⁻¹) (Supplementary Fig. 16c). The Li₂S nucleation capacity of FeNC-EEB-2 (196.8 mA h g⁻¹) is slightly higher than that of FeNC but lower than that of FeNC-EEB-1. During the potentiostatic charge at 2.35 V, the FeNC-EEB-1 exhibited a lower t_m (360 s) and higher Li₂S dissociation capacity (457.2 mA h g⁻¹) than FeNC (Fig. 3c and Supplementary Fig. 16d). The FeNC-EEB-2 also exhibited a lower t_m (489 s) and higher Li₂S dissociation capacity (381.5 mA h g⁻¹) than FeNC, but they were less effective than those of FeNC-EEB-1 (Supplementary Fig. 16e and f). *In situ* XRD analyses were further performed to directly characterize the Li₂S redox kinetics (Supplementary Fig. 17). During the first discharge/charge, FeNC-EEB-1 exhibited a highly reversible conversion reaction between S₈ and Li₂S (Fig. 3d and e). Especially, Li₂S nucleated and dissociated at the early stages of the B and C regions, respectively (Fig. 3f). Although FeNC-EEB-2 also exhibited reversible S₈ and Li₂S redox reactions (Supplementary Fig. 18), Li₂S nucleated and dissociated at a later stage of B and C than FeNC-EEB-1 (Fig. 3f). The overall Li₂S peak intensity of FeNC was lower than those of FeNC-EEB-1 and FeNC-EEB-2 owing to the lower Li₂S redox activity (Supplementary Fig. 19 and Fig. 3f). The Li₂S kinetic analyses

demonstrate that i) introducing $-\text{SO}_2/-\text{S}$ EEB sites adjacent to Fe-N-C improves the kinetics of the Li_2S -associated conversion reaction on Fe-N-C, and ii) EEB sites with low $-\text{SO}_2/-\text{S}$ ratios are more effective in promoting Li_2S nucleation/dissociation reactions on Fe-N-C catalysts than EEB sites with high $-\text{SO}_2/-\text{S}$ ratios.

To unveil the origin of the kinetic improvements of the Li_2S electrochemistry by EEB sites, DFT calculations were performed (Supplementary Fig. 20). Three model systems, namely, pristine Fe-N-C (FeNC), Fe-N-C with $-\text{S}$ species (FeNC-S), and Fe-N-C with $-\text{SO}_2$ species (FeNC- SO_2) were constructed to differentiate the effects of two different types of $-\text{S}$ and $-\text{SO}_2$ EEB sites on the electrocatalysis of Fe-N-C (Supplementary Fig. 20b). In all three models, Li atom of LiPS formed a bond with Fe atom in Fe-N-C. The calculated LiPS adsorption energy (E_{ad}) of FeNC-S was slightly lower (stronger adsorption strength) than that of FeNC, (Fig. 4a). This is attributed to the $-\text{S}$ species adjacent to Fe-N-C, increasing the Fe d -band center of Fe-N-C by their electron donating properties and thus resulting in the stronger adsorption to Fe of Li atom in LiPS (as demonstrated in Fig. 2g and Supplementary Fig. 14).^{39,40} In addition, the $-\text{S}$ species formed the moderate bond with Li atom of LiPS. However, although the downshifted Fe d -band center of Fe-N-C induced by electron withdrawing properties of neighboring $-\text{SO}_2$ species (as shown in Fig. 2g and Supplementary Fig. 14) is expected to increase the E_{ad} ,⁴¹ FeNC- SO_2 exhibits a much lower E_{ad} (stronger adsorption strength) than FeNC and FeNC-S (Fig. 4a). This is attributed to the $-\text{SO}_2$ species adjacent to Fe-N-C providing additional binding sites and forming quite strong bonds between O atoms of $-\text{SO}_2$ and Li atoms of LiPS (Fig. 4b and Supplementary Fig. 21c), which implies that the $-\text{SO}_2$ and $-\text{S}$ species that surround Fe-N-C exhibit completely different LiPS adsorption behaviors. Moreover, the change in the reaction energy (ΔE) was evaluated for each reaction pathway (Fig. 4c). First, ΔE value for the reduction of S_8 to Li_2S_8 indicates an exothermic reaction, and the subsequent four steps for the further reduction of Li_2S_8 to Li_2S through several intermediates (*i.e.*, Li_2S_6 , Li_2S_4 , and Li_2S_2) exhibit the coexistence of exothermic and endothermic reactions. Among these steps, the reduction reaction from Li_2S_4 to Li_2S exhibits the strong endothermic reaction in all the catalyst model systems, indicating that the kinetics of the sulfur reduction reaction is highly dependent on the energy barrier to nucleate the Li_2S from Li_2S_4 . For FeNC, ΔE for the reduction of Li_2S_4 to Li_2S is 1.41 eV (Fig. 4c and d). However, FeNC-S exhibits a lower ΔE (1.24 eV) than FeNC, whereas FeNC- SO_2 exhibits a higher ΔE (1.62 eV) than FeNC for the reduction of Li_2S_4 to Li_2S . These DFT calculations verify that both the $-\text{S}$ and $-\text{SO}_2$ species near Fe-N-C increase the adsorption strength of LiPS by providing additional binding sites and by modulating the Fe d -orbital level with electron exchange. Nevertheless, the $-\text{S}$ species which increase the LiPS adsorption strength to a moderate level, improve the Li-S electrochemistry kinetics on Fe SACs, whereas the $-\text{SO}_2$ species which increase the LiPS adsorption strength to a high level, deteriorate the Li-S electrochemistry kinetics on Fe-N-C (Fig. 4e). These DFT results support that the FeNC-EEB-1, with 5 times lower $-\text{SO}_2/-\text{S}$ ratio than FeNC-EEB-2, more effectively enhances the Li_2S electrocatalysis than FeNC-EEB-2.

Li-S performance in coin-cell configuration

Before fabricating the pouch cell, the coin-cell performance was investigated. Compared to mesoporous carbon (Supplementary Fig. 22a), FeNC exhibited a higher initial discharge capacity (1125 mA h g^{-1}) at a 0.2 C rate, owing to the electrocatalysis of Fe-N-C (Fig. 5a). FeNC-EEB-1 and FeNC-EEB-2 showed discharge capacities of 1324 and 1179 mA h g^{-1} , respectively, higher than those of FeNC. The polarization degree was also improved in FeNC-EEB-1 (0.17 V) and FeNC-EEB-2 (0.185 V), compared to that of FeNC (0.205 V) (Fig. 5b). Meanwhile, FeNC-EEB-1 exhibited a higher initial discharge capacity and lower polarization than FeNC-EEB-2, which was consistent with the results of the Li_2S kinetic studies. The cycle stability results show that mesoporous carbon exhibited only 627 mA h g^{-1} after 100 cycles (Supplementary Fig. 22b), whereas FeNC exhibited 864 mA h g^{-1} after 200 cycles (Supplementary Fig. 23). In FeNC-EEB-1, a discharge capacity of 1030 mA h g^{-1} ($\sim 20\%$ higher than FeNC) was retained after 200 cycles. FeNC-EEB-2 showed 925 mA h g^{-1} after 200 cycles, which was $\sim 7\%$ higher than that of FeNC, but $\sim 10\%$ lower than that of FeNC-EEB-1. Rate capabilities were also investigated at different current densities from 0.3 to 2.0 C rate (Fig. 5c). The FeNC-EEB-2 exhibited a slightly improved rate capability compared to FeNC, although FeNC-EEB-1 showed a highly improved capacity retention (78.4%) at a 2.0 C rate compared to FeNC (70.0%) and FeNC-EEB-2 (73.3%) (Supplementary Fig. 24). Additionally, FeNC-EEB-1 exhibited the lowest polarization at all currents (Supplementary Fig. 25a). In FeNC-EEB-2, the polarization was higher than FeNC-EEB-1, but lower than FeNC. Moreover, plateau discharge capacity (Q_L) fractions of FeNC-EEB-1 were higher than FeNC-EEB-2 and FeNC electrodes throughout all currents (Supplementary Fig. 25b), indicating that Li_2S_4 is most easily converted to Li_2S in FeNC-EEB-1. To further characterize the cathode state after cycling, time of secondary ion mass spectrometry (ToF-SIMS) analysis was performed. The S^- surface profile images of FeNC-EEB-1 and FeNC-EEB-2 represents weak intensities of secondary S^- ions (Fig. 5d), whereas FeNC exhibits a high-intensity S^- region owing to the many S agglomerates. Meanwhile, the ToF-SIMS depth profiles showed that the S^- intensities of cycled FeNC-EEB-1 and FeNC-EEB-2 increased as the sputtering time increased, while the S^- intensity decreased in FeNC (Fig. 5e), which agreed with ToF-SIMS 3D rendered images (Fig. 5f and Supplementary Fig. 26). This indicates that the S species are severely diffused and deposited on the external part of the electrode during cycling in FeNC owing to poor electrocatalysis (Supplementary Fig. 27). Conversely, the S species are well-preserved within the internal part of the electrode in FeNC-EEB-1 and FeNC-EEB-2 because the improved electrocatalysis inhibits the shuttle effect (Fig. 5g). These coin-cell studies suggest that introducing $-\text{SO}_2/-\text{S}$ EEB sites adjacent to the Fe-N-C catalysts promotes sulfur redox kinetics, achieving Li-S cells with high capacities, cycle stabilities, rate capabilities, and low polarizations (Supplementary Fig. 28). Especially, EEB sites with low $-\text{SO}_2/-\text{S}$ ratios are more suitable for efficiently enhancing the catalytic activity of Fe-N-C than those with high $-\text{SO}_2/-\text{S}$ ratios. This is because the $-\text{S}$ species near Fe-N-C moderately modulates the LiPS binding energy and lowers the energy barrier for the conversion reaction between Li_2S_4 and Li_2S compared to the $-\text{SO}_2$ species, which increases the LiPS binding energy too high.

Consequently, FeNC-EEB-1 exhibited ultrahigh cycle stabilities even at high current densities. At a 1.0 C rate, an initial discharge capacity of 1011 mA h g^{-1} was exhibited, and $\sim 80\%$ of the initial capacity (808 mA h g^{-1}) was retained even after 250 cycles, with a capacity decay ratio per cycle of only 0.08%

(Supplementary Fig. 29). Furthermore, FeNC-EEB-1 exhibited initial discharge capacities of 895 and 728 mA h g⁻¹ at a 2.0 and 3.0 C rate, respectively. After 250 cycles, 735 mA h g⁻¹ was maintained at a 2.0 C rate with a retention ratio of 82.1% and capacity decay ratio per cycle of 0.07%, whereas 495 mA h g⁻¹ was maintained even at a 3.0 C rate. To determine whether FeNC-EEB-1 can meet satisfactory levels of areal sulfur loading and E/S ratio and E/C ratios, a Li-S coin cell was operated under harsh conditions with an areal sulfur loading of 5.0 mg cm⁻² and an E/S ratio of 4.0 μ L mg⁻¹ (Fig. 5h). At a 0.1 C rate, the areal discharge capacity of 4.76 mA h cm⁻² (952 mA h g⁻¹) was exhibited with an E/C ratio of 4.2 μ L [mA h]⁻¹. Even after 100 cycles, the areal capacity of 4.06 mA h cm⁻² (812 mA h g⁻¹) was exhibited with an E/C ratio of 4.9 μ L [mA h]⁻¹. Despite the coin-cell configuration, a high-performance Li-S cell with low E/S ratio (4 μ L mg⁻¹) and E/C (4.2 μ L [mA h]⁻¹) ratios and a high areal sulfur loading (5.0 mg cm⁻²) were achieved by introducing -SO₂/S EEB sites to promote the electrocatalysis of Fe SACs (Supplementary Fig. 30 and Supplementary Table 2).

Fabrication of Li-S pouch cell

First, a 2.5 cm $\times$ 2.5 cm pouch cell was fabricated using a FeNC-EEB-1 cathode with a 3.6 mg cm⁻² S loading and 100 μ m Li metal anode (Supplementary Fig. 31). To satisfy the E/S ratio of 4.0 μ L mg⁻¹, the electrolyte content in the pouch cell was controlled to 58 wt% (Supplementary Fig. 32 and Supplementary Table 3). The as-fabricated pouch cell exhibited an initial discharge capacity of 1340 and 1117 mA h g⁻¹ at 0.18 and 0.36 mA cm⁻², respectively (Supplementary Fig. 33). Although this pouch cell exhibited a stable cycle life ($\sim$ 90% capacity retention) up to 20 cycles with an E/S ratio of 4.0 μ L mg⁻¹ at 0.18 mA cm⁻² (Fig. 6a), the W_G was limited to 160 W h kg⁻¹, owing to unsatisfactory levels of S loading in the cathode (only 5.6 wt% of the pouch cell as suggested in Supplementary Fig. 32), as well as N/P (4.3), and E/C (7.6 μ L [mA h]⁻¹) ratios. Considering the relationship between the total W_G , E/S ratio, and S loading, the pouch cells require S loadings > 8 mg cm⁻² and E/S ratios < 4.0 μ L mg⁻¹ to achieve a high W_G (> 300 W h kg⁻¹) (Fig. 6b). Therefore, we fabricated a 4 cm $\times$ 4 cm FeNC-EEB-1 cathode with a total S loading of 134.7 mg (8.4 mg cm⁻²) (Supplementary Fig. 34a). With an E/S ratio of 4.0 μ L mg⁻¹, the sulfur content in the pouch cell increased to 12.3 wt% and the electrolyte content decreased to 49.5 wt% (Supplementary Fig. 34b and Supplementary Table 4). The as-fabricated pouch cell showed an initial discharge capacity of 1258 mA h g⁻¹ (areal capacity of 10.6 mA h cm⁻²) at 0.42 mA cm⁻², achieving a high W_G of 325.4 W h kg⁻¹ with E/C and N/P ratios of 3.2 μ L [mA h]⁻¹ and 2.0 (only 100% excess Li), respectively (Supplementary Fig. 35 and Fig. 6c). The cell exhibited a stable cycle life for 80 cycles, maintaining a high Coulombic efficiency (> 95%). After 80 cycles, the discharge capacity was 906 mA h g⁻¹ with a 72% retention ratio of the initial capacity (Supplementary Fig. 36). In addition to the 325.4 W h kg⁻¹ pouch cell, we attempted to fabricate a Li-S pouch cell with an W_G higher than 350 W h kg⁻¹. The electrolyte amount added in the pouch cell was extremely decreased to satisfy an E/S ratio of 2.0 μ L mg⁻¹ (only 32.9 wt% of the pouch cell) (Supplementary Fig. 37 and Supplementary Table 5). The as-prepared 4 cm $\times$ 4 cm Li-S pouch cell featuring the FeNC-EEB-1 cathode with a S loading of 8.4 mg cm⁻² and an E/S ratio of 2.0 μ L mg⁻¹

exhibited an W_G of $361.8 \text{ W h kg}^{-1}$ and N/P ratio of 2.3 at the first cycle (Fig. 6d). Even after 10 cycles, the high W_G was maintained without a severe capacity decay (Supplementary Fig. 38). This outstanding Li-S pouch cell performance with the FeNC-EEB-1 cathode, compared with state-of-the-art pouch cell (Fig. 6e and Supplementary Table 6), is attributed to the design of highly active Fe SACs by manipulating their local environments with $-\text{SO}_2/-\text{S}$ EEB sites.

In summary, we proposed that the introduction of $-\text{SO}_2/-\text{S}$ EEB sites adjacent to Fe-N-C catalysts improves the adsorption strength of sulfur species and promotes the Li-S electrochemistry kinetics of the catalysts, achieving a high-energy Li-S pouch cell. The $-\text{SO}_2/-\text{S}$ EEB sites near the Fe-N-C catalysts function as additional binding sites for LiPS and exchange electrons with the Fe single atoms, modulating the Fe d -orbital level and LiPS E_{ads} of the Fe-N-C catalysts. Two different types of S species, $-\text{SO}_2$ and $-\text{S}$, show different LiPS adsorption characteristics and conversion behavior. In particular, the catalytic activity of Fe-N-C has a volcano relationship with the LiPS adsorption properties, and thus appropriate control of the $-\text{SO}_2/-\text{S}$ ratio of EEB sites allow sulfur species to adsorb moderately on the Fe single atoms, leading to favorable Li-S electrocatalysis of Fe-N-C. Consequently, high-energy Li-S pouch cell ($361.8 \text{ W h kg}^{-1}$) with low E/S ($2.0 \mu\text{L mg}^{-1}$) and E/C ($1.9 \mu\text{L [mA h]}^{-1}$) ratios was successfully fabricated. This study is the first to demonstrate a strategy to manipulate the local environment of SACs by EEB sites, which will create a promising avenue for the design of advanced SAC-based cathodes for high-energy Li-S pouch cells.

Method

Materials. Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123, M_n : ~ 5800), dibenzyl disulfide (DBDS, 98%), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$, 97%), furfuryl alcohol (98%), tetraethyl orthosilicate (TEOS, 99%), tetraethylene glycol dimethyl ether (TEGDME, 99%), sodium silicate, 1,10-phenanthroline (99%), and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 35.0~37.0%) and glacial acetic acid (99.8%) was obtained from SAMCHUN Pure Chemical Co. 1,3,5-Trimethylbenzene (mesitylene, 98%) was purchased from Merck Millipore and hydrofluoric acid (HF, 48.0~51.0%) was obtained from JT baker. Aluminum (III) chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) was purchased from Kanto Chemical Co. All chemicals were used as received without further purification.

Synthesis of mesoporous carbon (MSU-F-C). MSU-F-C was prepared with hard template method and utilized as porous carbon framework in cathode of Li-S cell. First, MSU-F- SiO_2 was prepared by sol-gel chemistry. P123 (9.6 mg) was dissolved in deionized (DI) water (160 ml) and glacial acetic acid (4.58 ml). Then, mesitylene (9.26 ml) was added in the solution and stirred for 1 h. A sodium silicate solution was also prepared by dissolving sodium silicate (15.5 ml) into DI water (240 ml). The sodium silicate solution was added in as-prepared P123 solution with stirring over 5 min, subsequently it was kept without stirring for 20 h at 40°C . The solution was aged in an oven at 100°C oven for 24 h. The aged solution was filtered and dissolved again in the mixture of DI water (200 ml) and HCl solution (5 ml). After 3 h, the above solution was filtered again and as-obtained product was calcined at 550°C for 4 h. After collecting

as-prepared MSU-F-SiO₂, it was dispersed in ethanol and AlCl₃·6H₂O (0.21 g) was added to obtain a homogeneous mixture. After drying in the oven at 60 °C to remove ethanol, the mixture was calcined at 550 °C for 4 h and Al-MSU-F-SiO₂ was obtained. The MSU-F-C was prepared by using Al-MSU-F-SiO₂ as a hard template and furfuryl alcohol was used as a carbon precursor. After wet-impregnation of furfuryl alcohol to Al-MSU-F-SiO₂, heat treatment was conducted at 850 °C for 4 h in Ar atmosphere. After cooling at room temperature, Al-MSU-F-SiO₂ template was etched by HF solution to obtain MSU-F-C.

Synthesis of FeNC, FeNC-EEB-1, and FeNC-EEB-2. To prepare FeNC-EEB-1, DBDS (768 mg) was dissolved in ethanol (100 ml). The appropriate amount of as-prepared DBDS solution was homogeneously impregnated into MSU-F-C with repetitive grinding until ethanol was completely evaporated. The DBDS-impregnated MSU-F-C was dried at 80 °C for 1 h, followed by heat treatment at 900 °C for 1 h in Ar atmosphere to generate low -SO₂/-S ratio EEB sites. For the formation of Fe-N-C catalysts into EEB sites-embedded MSU-F-C, Fe-N-C precursor solution was firstly prepared by dissolving FeCl₃·6H₂O and 1, 10-phenanthroline in ethanol. Then, this precursor solution was wet-impregnated into EEB sites embedded MSU-F-C with vigorous grinding. The mixture was dried at 80 °C for 1 h, followed by heat treatment at 900 °C for 1 h in Ar atmosphere. After cooling at room temperature, product was stirred in 1 M HCl solution to remove aggregated Fe metal residue, and FeNC-EEB-1 was obtained. The FeNC-EEB-2 was prepared by same method with FeNC-EEB-1, but using Na₂S₂O₅ to generate EEB sites instead of DBDS. The FeNC was also prepared by same method without the process for the generation of EEB sites.

Material characterization. A transmission electron microscopy (TEM; G2 F30 S-Twin, Tencai) and a scanning electron microscopy (SEM; S-4800 field emission, Hitachi) were used to observe the particle morphologies and porous structures of as-synthesized materials. The porous structure was further analyzed by nitrogen physisorption analysis at 77 K using a Micromeritics Tristar II 3020 system. X-ray diffraction (XRD) patterns were obtained using a RIGAKU D/MAX-2500V X-ray diffractometer (Cu K_α radiation, λ = 1.541 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed using VG Scientific Escalab 250 (Al K_α). High annular dark-field scanning TEM (STEM) and energy dispersive spectroscopy (EDS) were conducted for the detection of Fe single atom and further elemental distribution investigation by using a High-resolution TEM (HR-TEM; Titan cubed G2 60-300). X-ray absorption spectroscopy (XAS) analysis was performed at the 7D XAFS beamline at Pohang Accelerator Laboratory (PAL, Korea) to characterize the electronic structures of each Fe-N-C catalysts. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analyses were performed with Cs⁺ sputter condition (5 keV, 35 nA) and Bi⁺ analysis condition (30 keV, 1 pA).

Computational details. Density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP).^{42,43} The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and projector augmented-wave (PAW) pseudo-potential were adopted with spin polarization.^{44,45} FeNC models, force and energy criteria for structure optimization, k-point grid, plane wave cutoff and adsorption energy definitions are the same as in our previous study.³⁴ The geometries of

S₈ and Li₂S_n species (n = 8, 6, 4, 2, and 1) refers the previous theoretical studies^{46,47} and they were re-optimized in 20 × 20 × 20 Å³ box to calculate the gas-phase energy.

Fabrication of Li-S coin cell and characterization. A composites of sulfur (70 wt%) with FeNC, FeNC-EEB-1, and FeNC-EEB-2 were prepared by heating the mixture at 155 °C for 8 h. To fabricate the working electrodes, a slurry was prepared by mixing the sulfur composite with each catalysts materials and polymeric binder (polyvinylidene difluoride, PVDF) in a weight ratio of 9:1 using a solvent (*N*-methyl-2-pyrrolidone, NMP). The prepared slurry was coated on carbon coated Al foil, and dried at 60 °C for 8 h. Subsequently, the electrode was pressed and cut into a coin-shape. A porous polypropylene membrane (Celgard 2400, Welcos Ltd) was used as the separator. The electrochemical performance was measured using a coin-type cell (CR2032), and lithium metal with 200 μm thickness was used as both the reference and counter electrodes. A solution containing 1.0 M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) in a mixed solvent of dimethoxymethane and 1,3-dioxolane (DME/DOL, 1:1 volume ratio, PANAX E-TEC Co., Korea) with 2.0 wt.% of lithium nitrate (LiNO₃, 99.99% metal basis, Sigma-Aldrich) as an additive was used as an electrolyte. The average areal sulfur loading was controlled at 2.0 mg cm⁻² and E/S ratio was fixed to 10 μL mg⁻¹ for the Li₂S nucleation/dissociation kinetic studies and coin-cell test at mild condition. For the coin cell test at harsh condition, electrodes with areal sulfur loading of 1.5-5.0 mg cm⁻² was fabricated and tested with E/S ratio of 4.0 μL mg⁻¹. Galvanostatic charge-discharge analysis was performed in the potential range between 1.7 and 2.8 V (vs. Li/Li⁺) at different current densities from 0.2 to 3.0 C rate (1 C rate ~1675 mA g⁻¹). The capacity was calculated based on the sulfur weight in the electrode. Cyclic voltammetry (CV) was conducted with scan rate of 0.2 mV s⁻¹ in the potential range of 1.5-3.2 V (vs. Li/Li⁺). For the *in situ* XRD analysis, 2032 type coin cell with 1.5 mm hole was designed and used for collecting the 2D mode XRD patterns. The sulfur loading and E/S ratio for *in situ* XRD analysis were fixed to 2.0 mg cm⁻² and 10 μL mg⁻¹. Each electrode was galvanostatically discharged and charged at 0.2 C rate to clearly differentiate the Li₂S redox kinetics. All the *in situ* XRD data were collected at Korea Advanced Institute of Science and Technology Analysis Center for Research Advancement (KARA).

Fabrication of Li-S pouch cell and characterization. A composites of FeNC-EEB-1 (30 wt%) and sulfur (70 wt%) was prepared by same method (melt-diffusion) with Li-S coin-cell. To fabricate the working electrodes, a slurry was prepared by mixing the FeNC-EEB-1/sulfur composite and LA132 binder in a weight ratio of 9:1 using a solvent (DI water). The prepared slurry was coated on carbon coated Al foil (20 μm), and dried at 60 °C for 8 h. Subsequently, the electrode was cut into 2.5 cm × 2.5 cm and 4 cm × 4 cm shape. For the fabrication of Li-S pouch cell, Cu foil with 10 μm was used as current collector for Li metal anode (thickness of 100 μm). The Celgard 2400 was used as a separator and pre-immersed in electrolyte for 6 h before the fabrication of Li-S pouch cell. Al and Ni tab was pasted to Cu and Al current collectors for applying and measuring current and potential. For the fabrication of 2.5 cm × 2.5 cm Li-S pouch cell, areal sulfur loading in cathode was fixed to 3.6 mg cm⁻². The electrolyte amount was carefully calculated and used to achieve E/S ratio of 4.0 μL mg⁻¹. For the fabrication of 4 cm × 4 cm Li-S pouch cell, areal sulfur loading in cathode was fixed to 8.4 mg cm⁻² and the electrolyte amount was controlled to

achieve E/S ratio of 2.0 and 4.0 $\mu\text{L mg}^{-1}$. The Li-S pouch cell was electrochemically tested at 30 °C and specific capacity was calculated based on the amount of sulfur in cathode.

The total gravimetric energy density (W_G) of Li-S pouch cell was evaluated by below equations:

$$W_G = \frac{QV}{\sum M_j}$$

Where Q and V indicates the capacity (mA h) and average operating voltage (V), respectively and M_j is the weight (g) of all component of the Li-S pouch cell. The M_j includes the weight of Cu current collector, Li metal, separator, electrolyte, sulfur, binder, carbon/catalysts composite, and Al current collector.

Declarations

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Author contributions

W.-G. Lim, C.-Y Park, H. Jung, J. W. Han and J. Lee conceived the research concept. W.-G. Lim, C.-Y Park and J. Lee designed the experiments and analyzed the results. H. Jung and J. W. Han performed DFT calculations and analysis. S. Kim, S. H. Kang, Y.-G. Lee, Y. C. Jeong, S. B. Yang and K. Sohn contributed to the scientific discussion and results analysis. W.-G. Lim, C.-Y Park, H. Jung, J. W. Han and J. Lee wrote the manuscript. J. W. Han and J. Lee supervised the project. All authors commented on the manuscript.

Competing interests

The authors declare that they have no competing interests.

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Figures

Figure 1

(a) Schematic description of electron exchangeable binding (EEB) sites near Fe-N-C catalysts. The Li-S electrochemistry on Fe SACs is enhanced by controlling the LiPS adsorption properties; EEB sites provide additional binding sites by the forming bonds with LiPS species (function 1) and also modulate Fe *d*-orbital level by the electron exchange with Fe-N-C catalysts (function 2). (b) Schematic presentation of the fabrication process for a high-energy Li-S pouch cell satisfying low E/S, N/P, and E/C ratios.

Figure 2

(a) Schematic description of the synthetic process to prepare $-\text{SO}_2/-\text{S}$ EEB sites-assisted Fe-N-C catalysts. (b) XPS S 2p spectrum of FeNC-EEB-1 and (c) FeNC-EEB-2. (d) Fe contents measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and $-\text{SO}_2/-\text{S}$ ratios of FeNC, FeNC-EEB-1, and FeNC-EEB-2. (e) STEM image of FeNC-EEB-1. Fe single atoms are highlighted by white circles. (f) FT-EXAFS spectra of the reference Fe foil, FeNC, FeNC-EEB-1, and FeNC-EEB-2. (g) Magnified white line of Fe K-edge XANES in FeNC, FeNC-EEB-1, and FeNC-EEB-2. Shift of the white line intensity is attributed to the electron density change of Fe single atoms (*i.e.*, shift of Fe *d*-band center) by electron exchange with neighboring $-\text{SO}_2/-\text{S}$ EEB sites.

Figure 3

(a) Tafel plots for cathodic and anodic reactions of FeNC, FeNC-EEB-1, and FeNC-EEB-2. (b) Potentiostatic discharge curves of FeNC-EEB-1 at 2.05 V. (c) Potentiostatic charge curves of FeNC-EEB-1 at 2.35 V. (d) *In situ* XRD patterns of FeNC-EEB-1 for the first discharge/charge process at a 0.2 C rate. Crystalline peaks of S_8 and Li_2S correspond to orthorhombic (JCPDS No. 00-008-0247) and cubic (JCPDS No. 00-023-0369) phases, respectively. (e) Magnified *in situ* XRD patterns of FeNC-EEB-1 in the region of Li_2S nucleation and dissociation. (f) Contour *in situ* XRD images and corresponding voltage profiles of FeNC-EEB-1, FeNC-EEB-2, and FeNC electrodes. For these Li_2S nucleation/dissociation kinetic studies, the areal sulfur loading in the cathode and the E/S ratio was fixed to 2.0 mg cm^{-2} and $10 \mu\text{L mg}^{-1}$, respectively.

Figure 4

(a) Calculated adsorption energies of LiPS species on FeNC, FeNC-S, and FeNC-SO₂. (b) Molecular configuration of Li_2S_4 adsorption on FeNC-SO₂. (c) Relative energy diagrams for the sulfur conversion reaction. (d) Calculated ΔE values for the conversion steps of Li_2S_4 to Li_2S in FeNC, FeNC-S, and FeNC-SO₂. (e) Schematics of LiPS adsorption and conversion behaviors on Fe-N-C catalysts with different local environments.

Figure 5

(a) Initial voltage profiles of FeNC, FeNC-EEB-1, and FeNC-EEB-2 at the 0.2 C rate. (b) Summary of the discharge capacities and polarization potentials at the 0.2 C rate. (c) Rate capabilities of FeNC, FeNC-EEB-1, and FeNC-EEB-2 with different current densities from the 0.3 to 2.0 C rate. For all the coin-cell studies in (a-c), the electrode with a sulfur areal loading of 2.0 mg cm⁻² and E/S ratio of 10 μL mg⁻¹ was utilized. (d) ToF-SIMS S⁻ ion mappings on the top surface and (e) ToF-SIMS depth profiles of each electrode after operating 20 cycles at a 0.2 C rate. (f) ToF-SIMS 3D rendering S⁻ depth profile image of the cycled FeNC-EEB-1 electrode. (g) Schematics of the LiPS dissolution behavior in EEB sites-embedded S cathode. (h) Cycle performance of FeNC-EEB-1 at a 0.1 C rate with different sulfur areal loadings. FeNC-EEB-1 exhibited 1300 mA h g⁻¹ (1.95 mA h cm⁻²) with a S loading of 1.5 mg cm⁻² and 1166 mA h g⁻¹ (4.08 mA h cm⁻²) with a S loading of 3.5 mg cm⁻². Pre-cycling for 5 cycles at a 0.02 C rate was performed before the cycling at a 0.1 C rate and the E/S ratio was fixed to 4.0 μL mg⁻¹.

Figure 6

(a) Galvanostatic test results of a 2.5 cm × 2.5 cm Li-S pouch cell at 0.18 mA cm⁻². (b) Calculated correlation plot of W_G with the E/S ratio and sulfur areal loading. For the calculation, the capacity and average potential were fixed to 1200 mA h g⁻¹ and 2.1 V, respectively. (c) Galvanostatic test results of the 4 cm × 4 cm Li-S pouch cell with an E/S ratio of 4.0 μL mg⁻¹ at 0.42 mA cm⁻². (d) Initial voltage profiles of

the 4 cm ´ 4 cm Li-S pouch cell with an E/S ratio of 2.0 µL mg⁻¹ at 0.42 mA cm⁻². (e) Comparison of the Li-S pouch cell performance with recently reported studies.

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