Supporting information for:

**Theoretical consideration of side reactions between the VS4 electrode and carbonate solvents in lithium–metal polysulfide batteries**

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**S1. Decomposition Products and Broken Bond Positions for DMC and PC Solvents**

Figures S1 and S2 show molecular structures of assumed decomposition products and bond positions to be broken for DMC and PC molecules, respectively.

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Figure S1: Molecular structures of considered decomposition products and assumed bonds to be broken for DMC. Green lines denote broken bond positions. The products labeled by D1-D4 and D5-D7 are from singly and doubly reacting molecules, respectively.

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Figure S2: Molecular structures of considered decomposition products and assumed bonds to be broken for PC. Purple lines denote broken bond positions. The products labeled by P1-P4 and P5-P7 are from singly and doubly reacting molecules, respectively.

**S2. Detailed Method for Calculating the Change in the Gibbs Free Energy and Equilibrium Potential for Decomposition Reactions**

In this section, we describe the calculation method for the change in the Gibbs free energy Δ*G* using the thermodynamic method, and the equilibrium potential *V*eq using the electromotive force (EMF) formula for the decomposition reactions.

**S2.1. Change in the Gibbs Free Energy Δ*G* using the Thermodynamic Method**

In the Δ*G*1 calculation, we used the total energy *E*DFT obtained by the first-principles density functional theory (DFT) for Δ*G* calculation as follows:

Δ*G*1 = *E*DFT(Li2S) − 2*E*DFT(Li) – 1 / 128*E*DFT(S128). (S1)

Here, we assumed that Li2S, Li, and S128 are in their solid states, and the *α*-S bulk for the solid state of S128, which contains 128 S atoms in the unit cell. S1 Note that the pressure and entropy terms are neglected in Eq. (S1).

Δ*G*1 can be converted to the electromotive force (EMF) *E*EMF as follows:

*E*EMF = Δ*G*1 / *nF*, (S2)

where *n* and *F* indicate the number of reacted electrons and the Faraday constant, respectively. The result of *E*EMF [V vs. Li/Li+] is 2.12 V. This result agrees well with the average EMF (2.15 V) of the lithium sulfur battery.S2

Δ*G*2 can be represented as follows:

Δ*G*2 = Δ*G*at(Li) + Δ*G*at(S) − Δ*G*solv(EC). (S3)

Here, Δ*G*at(Li), Δ*G*at(S), and Δ*G*solv(EC) denote the atomization free energies for Li and S, and the solvation free energy for EC. We calculated Δ*G*at as the difference in the *E*DFT between the isolated atomic and solid states. Note that, to determine Δ*G*at(Li) and Δ*G*at(S), the experimental value of the standard molar entropy term that is taken from the thermodynamic tableS3 is added to *E*DFT for the isolated atoms. The results of Δ*G*at(Li) and Δ*G*at(S) are respectively 1.22 eV and 2.82 eV, which are respectively in good agreement with the experimental values of 1.31 eV and 2.45 eV.S4 Δ*G*solv(EC) is determined by the one-dimensional reference interaction site model (1D-RISM). We did not consider the special correction terms for Δ*G*solv, because the entropic contribution is included in Δ*G*solv(EC) within the RISM theory.S5–S7 The result of Δ*G*solv(EC) is −0.39 eV, which is in reasonable agreement with the range of the theoretical values from −0.36 eV to −0.50 eVS8, S9.

Δ*G*3 and Δ*G*4 correspond to the gas-phase formation and solvation free energies of the decomposition products, respectively. For Δ*G*3, the zero-point vibration and translational and rotational energies are included in the total energy. Pressure and standard molar entropy terms are calculated by the equation of states for the ideal gas formulated under the canonical ensemble, which are added to the total energy to determine the Gibbs free energy. All thermodynamic parameters for the gas-phase atoms and molecules were calculated at the temperature of 298.15 K. Δ*G*4, which corresponds to Δ*G*solv(EC) for the decomposition product, were evaluated by 1D-RISM calculations.

**S2.2. The Equilibrium Potential *V*eq using Electromotive Force Formula**

Here, we describe details of *V*eq calculation with Eq. (1) using electrochemical reactions discussed in section 2.4. The Gibbs free energies for left and right components (*G*L and *G*R) in reaction 3 can be written as follows, respectively:

*G*L = *G*(VS4) + *G*(EC) + 3*G*(Li), (S4)

*G*R = *G*(C3O3H4SLi2) + *G*(LiVS3). (S5)

Since Δ*G* in Eq. (1) is obtained by the difference between *G*L and *G*R, equations (S4) and (S5) can be combined with Eq. (1), and then we obtain

*V*eq = −[*G*(C3O3H4SLi2) + *G*(LiVS3) – {*G*(VS4) + *G*(EC) + 3*G*(Li)}] / *nF*

= {*G*(VS4) + *G*(EC) + 3*G*(Li) – *G*(C3O3H4SLi2) – *G*(LiVS3)} / *nF*. (S6)

By using the above procedure and Li negative electrode, we also obtain EMF for reaction 4 *E*EMF(4) vs. Li/Li+ as follows:

*E*EMF(4) = {*G*(VS4) + 3*G*(Li) – *G*(Li2S) – *G*(LiVS3)} / *nF*. (S7)

By Eq. (S7), Eq. (S6) can be re-written as

*V*eq = *E*EMF(4) +{*G*(Li2S) + *G*(EC) – *G*(C3O3H4SLi2)} / *nF*. (S8)

The second term on the right-hand side in Eq. (S8) corresponds to the negative value of the change in the Gibbs free energy Δ*G* for reaction 5 divided by *nF*, which is obtained by the thermodynamic cycle discussed in sections 2.4 and S3.2. Therefore, we calculate *V*eq for the decomposition reaction referencing to the Li/Li+ potential by the following simple form:

*V*eq = *E*EMF(4) – Δ*G* / *nF*. (S9)

**S3. Computational Details for Calculations with Quantum ESPRESSO**

Here, we provide computational details for the calculations of the Quantum ESPRESSO. S10, S11 Cut-off energies for the wavefunctions and augmented charges were 50 Ry and 400 Ry, respectively. For the Li bulk and atom, we used 80 Ry and 640 Ry as the cut-off energies for the wavefunctions and augmented charges, respectively. We performed the structure optimization until the forces acting on the atoms became smaller than 1.0×10-3 Ry/Bohr. Cell optimization was also carried out with the criteria of 0.5 Kbar. We summarize the ***k***-point samplings and spin-states used in this study, as well as the optimized lattice parameters shown in Table S1. Here, NM, FM, and AFM denote the non-magnetic, ferromagnetic, and antiferromagnetic states, respectively. For Li and Li2S, we only show the results of the lattice constants for the *a*-axes due to the symmetry of the lattice structures. Figure S3 shows the optimized crystal structures. In this study, we used ultrasoft-pseudopotentialS12-S14 within the nonlinear core correction schemeS15 for the valence-core interaction. The valence electron configurations for the Li, S, and V atoms were 1*s*22*s*1, 3*s*23*p*4, and 3*s*24*s*23*p*63*d*3, respectively. For isolated Li and S atoms, a unit cell with a size of 20×20×20 Å3, and only the Γ-point was adopted for the ***k***-point sampling.

Table S1: Summary of ***k***-point samplings, structures, spin-states and optimized lattice parameters for Li, Li2S, *α*-S, VS4, Li3VS4 and LiVS3. The experimental lattice parameters taken from the AtomWork database are also shown in parenthesesS16. Note that, for Li3VS4 and LiVS3, we show the initial lattice parameter taken from the Materials Project database in parenthesesS17.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | *k*-points | Structure  (space group) | Spin | *a* [Å] | *b* [Å] | *c* [Å] |
| Li | 12×12×12 | BCC | NM | 3.429 (3.436) |  |  |
| Li2S | 12×12×12 | Fluorite  (*Fm-3m*) | NM | 5.694 (5.715) |  |  |
| *α*-S | 2×2×1 | Orthorhombic  (*Fddd*) | NM | 10.319 (10.46) | 12.777 (12.837) | 24.399 (24.417) |
| VS4 | 4×4×4 | Monoclinic  (*C2/c*) | AFM | 6.771 (6.78) | 8.250 (8.2215) | 8.250 (8.2215) |
| Li3VS4 | 8×8×8 | Cubic  (*P43m*) | NM | 5.894 (5.955) |  |  |
| LiVS3 | 8×8×8 | Triclinic  (*P1*) | FM | 5.873 (5.808) | 6.337 (6.487) | 6.696 (6.670) |

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Figure S3: Optimized crystal structures of Li, Li2S, *α*-S, VS4 and LiVS3.

**S4. Determination of *U* parameter for 3*d*-orbital of the Vanadium Atom**

We used the DFT + *U* methodS18 for the 3*d*-orbital of the vanadium atom. In this study, we adjusted the value of the Hubbard *U* parameter to reproduce the experimental lattice parameters and bandgap *E*g of the VS4 bulk. Table S2 shows the results of lattice parameters and *E*g for VS4 with changes in the value of *U*. Here, we used NM, FM, and AFM states for initial spin polarization. For *U* = 0.0 eV, all magnetic states show the same result. We checked the values of the magnetic moment, and zero magnetic moments were found for all initial spin states. When the DFT + *U* calculation was switched on, the AFM state showed a lower total energy. Thus, the AFM state is the grand-state of VS4 at the finite value of *U*. For *U* = 1.0 eV in the AFM state, the lattice parameter results agree well with the experimental data; however, *E*g is underestimated compared to the experiment. The lattice parameters and *E*g for *U* = 2.0 eV in the AFM state reproduce the experimental data well. For *U* = 3.0 eV, the lattice parameter results deviate slightly from the experiment, and *E*g is overestimated. From the above discussion, we used the value of *U* = 2.0 eV throughout this paper.

Table S2: The results of lattice parameters, band-gap energy *E*g and total energy *E*DFT for VS4 with various combinations of *U* parameter and spin-states.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *U* [eV] | Spin | *a* [Å] | *b* [Å] | *c* [Å] | *α* [°] | *β* [°] | *γ* [°] | *E*g [eV] | *E*DFT [Ry] |
| 0.0 | NM | 6.761 | 8.171 | 8.171 | 78.8 | 73.5 | 73.5 | 0.84 | −948.852 |
| FM | 6.762 | 8.171 | 8.171 | 78.8 | 73.5 | 73.5 | 0.84 | −948.852 |
| AFM | 6.761 | 8.171 | 8.171 | 78.8 | 73.5 | 73.5 | 0.84 | −948.852 |
| 1.0 | NM | 6.766 | 8.175 | 8.175 | 78.8 | 73.5 | 73.5 | 0.92 | −948.489 |
| FM | 6.770 | 8.175 | 8.175 | 78.9 | 73.5 | 73.5 | 0.92 | −948.489 |
| AFM | 6.764 | 8.216 | 8.216 | 78.0 | 73.7 | 73.7 | 0.99 | −948.500 |
| 2.0 | NM | 6.766 | 8.185 | 8.185 | 78.7 | 73.3 | 73.3 | 0.93 | −948.127 |
| FM | 6.740 | 8.290 | 8.290 | 76.3 | 75.0 | 75.0 | 0.97 | −948.131 |
| AFM | 6.771 | 8.250 | 8.250 | 77.4 | 73.9 | 73.9 | 1.36 | −948.173 |
| 3.0 | NM | 6.771 | 8.191 | 8.191 | 78.7 | 73.2 | 73.2 | 0.95 | −947.766 |
| FM | 6.805 | 8.348 | 8.348 | 76.3 | 75.2 | 75.2 | 1.37 | −947.829 |
| AFM | 6.767 | 8.297 | 8.297 | 76.9 | 74.3 | 74.3 | 1.48 | −947.858 |
| Expt. | -- | 6.78a | 8.2217a | 8.2215a | 78.647a | 74.056a | 74.056a | 1.35b | -- |

a: Taken from Ref. S16, b: Taken from Ref. S19

**S5. Results of Change in the Gibbs Free Energies for Decomposition Reactions**

Table S3 shows the decomposition reactions and the corresponding results of Δ*G*, which are the original data for Fig. 5(a)−(c) in the manuscript.

Table S3: Results of Δ*G* for all decomposition reactions unit in eV.

|  |  |  |
| --- | --- | --- |
| Label | Decomposition Reactions | Δ*G* [eV] |
| E1 | Li2S(solid) + EC(solv) → C3O3H4SLi2(solv) | −0.47 |
| E2 | Li2S(solid) + EC(solv) → Li2CO3(solv) + C2H4S(solv) | −0.80 |
| E3 | Li2S(solid) + EC(solv) → Li2CO3(solv) + C2H2(gas) + H2S(gas) | +0.40 |
| E4 | Li2S(solid) + EC(solv) → CO2(gas) + C2OH4SLi2(solv) | +0.63 |
| E5 | Li2S(solid) + 2EC(solv) → C6O6H8SLi2(solv) | −1.49 |
| E6 | Li2S(solid) + 2EC(solv) → C4O6H4Li2(solv) + C2H4S(solv) | −1.06 |
| E7 | Li2S(solid) + 2EC(solv) → C4O6H4Li2(solv) + C2H2(gas) + H2S(gas) | +0.13 |
| D1 | Li2S(solid) + DMC(solv) → C2O3H3Li(solv) + LiCH3S(solv) | +0.83 |
| D2 | Li2S(solid) + DMC(solv) → Li2CO3(solv) + (CH3)2S(solv) | −0.31 |
| D3 | Li2S(solid) + DMC(solv) → Li2CO3(solv) + C2H4(gas) + H2S(gas) | −1.38 |
| D4 | Li2S(solid) + DMC(solv) → CO2(gas) + LiCH3O(solv) + LiCH3S(solv) | −0.82 |
| D5 | Li2S(solid) + 2DMC(solv) → 2C2O3H3Li(solv) + (CH3)2S(solv) | −1.68 |
| D6 | Li2S(solid) + 2DMC(solv) → C4O6H4Li2(solv) + C2H6(gas) + H2S(gas) | −1.90 |
| D7 | Li2S(solid) + 2DMC(solv) → C6O6H10S(solv) + 2LiH(solv) | +4.93 |
| P1 | Li2S(solid) + PC(solv) → C4O3H6SLi2(solv) | −0.25 |
| P2 | Li2S(solid) + PC(solv) → Li2CO3(solv) + C3H6S(solv) | −0.76 |
| P3 | Li2S(solid) + PC(solv) → Li2CO3(solv) + C3H4(gas) + H2S(gas) | +0.49 |
| P4 | Li2S(solid) + PC(solv) → CO2(gas) + C3H6OSLi2(solv) | −0.28 |
| P5 | Li2S(solid) + 2PC(solv) → C8O6H12SLi2(solv) | −1.23 |
| P6 | Li2S(solid) + 2PC(solv) → C5O6H6Li2(solv) + C3H6S(gas) | −0.87 |
| P7 | Li2S(solid) + 2PC(solv) → C5O6H6Li2(solv) + C3H4(gas) + H2S(gas) | +0.38 |

**S6. Experimental Results of LC-MS Analysis**

We carried out the experiment of LC-MSS20, a VS4/Li battery with 1M-LiPF6 EC/DMC (1:1 vol%) and EC/PC (1:1 vol%), to investigate the qualitative features of sulfur-containing decomposition products. Here, we focus on LC-MS components containing VS4 electrode materials, such as vanadium and sulfur. The experimental conditions and procedures are explained as follows.

First, after the 10th discharge/charge cycle, we took a battery cell apart in the glove box under an Ar atmosphere and collected the electrolyte solutions. The electrolyte solutions were then diluted with super-dehydrated acetonitrile in a glove box under N2 atmosphere. Finally, we measured the mass spectra using high-performance LC-MS. As the reference sample of electrolyte solutions, we also carried out LC-MS analysis on pure 1M-LiPF6 EC/DMC and EC/PC solutions. Liquid chromatography and mass spectrometry were carried out using Nexera X2 (Shimazu Corporation) and TripleTOF 5600+ (AB Sciex Pte. Ltd, respectively). The mass spectrum was observed in the range of 50–1000 m/z. When the intensity of the mass spectrum was sufficient for further analysis, we carried out LC-MS/MS analysis to more precisely estimate the chemical formulae of sulfur-containing decomposition products.

For the battery cycle test, we used the VS4 based composite consisting of the VS4/KB/binder, with a weight ratio of 85.3: 10.7: 4 as a positive electrode and a coating weight of 3.2 mg/cm2. The discharge/charge cycle test was carried out in a voltage range of 1.5−2.6 V utilizing a discharge/charge rate of 0.1 C.

Figure S4(a) and (b) show the results of the total ion chromatogram (TIC) for the 1M-LiPF6 EC/DMC solution before and after the battery cycles, respectively. Here, we only show the TIC for 1M-LiPF6 EC/DMC as a representative of LC-MS data. We observed a change in the TIC between the reference sample and the sample after the 10th discharge/charge cycle. By mass analysis, we obtained the signal from the sulfur-containing decomposition products of organic solvents. The formulae of the decomposition products found in 1M-LiPF6 EC/DMC and 1M-LiPF6 EC/PC are listed in Tables S4 and S5, respectively. For the EC/DMC solution, the detected decomposition products are referred to as carbonate-based structures with one or two sulfur atoms, where the sulfur atoms are from the VS4 electrode. For the EC/PC solution, the decomposition products were similar to those for EC/DMC. In addition, we identified the decomposition product derived from the decomposed LiPF6 in peak No. 2.

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Figure S4: Total ion chromatogram (TIC) of 1M-LiPF6 EC/DMC solution (a) for reference sample and (b) for the solution after the battery cycles. Time of flight with a range from 0 to 30 min. is shown.

Table. S4: The sulfur contained decomposition products of organic solvents detected by LC-MS and LC-MS/MS analysis for 1M-LiPF6 EC/DMC. The peak No. was in the descending order of the mass spectrum intensity including sulfur component. Time-of-flight (TOF) in min., intensity, ionic mass per the number of ionic charges (*m/z*) and estimated chemical formula are listed.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | TOF [min.] | Intensity | *m*/*z* | Chemical formula |
| 1 | 13.4 | 2008248 | 372.13 | C13H22O9S |
| 2 | 13.4 | 1700418 | 344.10 | C11H18O9S |
| 3 | 14.2 | 656949 | 316.08 | C10H18O6S2 |
| 4 | 14.2 | 645427 | 344.11 | C12H22O6S2 |
| 5 | 14.8 | 578496 | 432.13 | C15H26O9S2 |

Table. S5: The sulfur contained decomposition products of organic solvents detected by LC-MS and LC-MS/MS analysis for 1M-LiPF6 EC/PC. The peak No. was in the descending order of the mass spectrum intensity including sulfur component. Time-of-flight (TOF) in min., intensity, ionic mass per the number of ionic charges (*m/z*) and estimated chemical formula are listed.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | TOF [min.] | Intensity | *m*/*z* | Chemical formula |
| 1 | 10.5 | 13853 | 316.12 | C11H22O5S2 |
| 2 | 12.0 | 11852 | 376.12 | C13H23O6FS2 |
| 3 | 10.5 | 6034 | 293.04 | C9H18O5S2 |
| 4 | 10.7 | 5213 | 225.04 | C7H12O6S |
| 5 | 12.3 | 4731 | 285.04 | C9H16O6S2 |

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S-3

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