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A High-Capacity Lithium – Gas Battery Based on Sulfur Fluoride Conversion

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ABSTRACT

Identification of novel redox reactions that combine the prospects of high potential and capacity can contribute new opportunities in the development of advanced batteries with significantly higher energy density than today’s state of the art, while advancing current understanding of nonaqueous electrochemical transformations and reaction mechanisms. The immense research efforts directed in recent years towards metal-gas, and in particular lithium-oxygen (Li-O2) batteries, have highlighted the role that gas-to-solid conversion reactions can play in future energy technologies; however, efforts have mainly focused on tailoring the anode (alkali metal) in the metal-gas couple to achieve improved reversibility. Here, in a different approach, we introduce and characterize a new gas cathode reaction that capitalizes on the full change in oxidation state (from +6 to -2) available in redox-active sulfur, based on the cathodic reduction of
highly fluorinated sulfur hexafluoride (SF₆) in a Li metal battery. In glyme-based electrolyte (0.3 M LiClO₄ in TEGDME), we establish, using quantitative gas and ¹⁹F NMR analysis, that discharge predominantly involves an 8-electron reduction of SF₆, yielding stoichiometric LiF, as well as Li₂S and modest amounts of higher-order Li polysulfides. This multi-phase conversion reaction yields capacities of ~3600 mAh g⁻¹ at moderate rates (30 mA g⁻¹) and potentials up to 2.2 V vs. Li/Li⁺. In a non-glyme electrolyte, 0.3 M LiClO₄ in DMSO, SF₆ reduction also proceeds readily, yielding higher capacities of ~7800 mAh g⁻¹ at 30 mA g⁻¹. Although not at present rechargeable, the demonstration of, and insights gained, from the primary Li-SF₆ system provides a promising first step for design of novel sulfur conversion chemistries with energy densities that exceed those of today’s Li primary batteries, while demonstrating a new design space for nonaqueous gas-to-solid electrochemical reactions.
INTRODUCTION

Nonaqueous metal-gas batteries have received immense focus in recent years owing to their potential to contribute to growing demands for high energy density batteries that can compete with or exceed the energy density of today’s Li-ion systems.1–2 Among these, the lithium-oxygen (Li-O₂) battery in particular has received the lion’s share of research attention. However, substantial challenges in the rechargeability and cycle life of Li-O₂ batteries have tempered once-high expectations that they can meet needs for electric vehicles in the near term.3 Regardless of the long-term prognosis of rechargeable O₂-based systems, substantial progress has been made in the fundamental science and engineering of metal-gas electrochemical reactions as a result of these efforts, and the metal-gas family has expanded dramatically to now include, among others, the Na-O₂,4–5 K-O₂,6 Mg-O₂,7 Ca-O₂,8 rechargeable Li-SO₂,9 and Li-CO₂ batteries.10–11 This progress has yielded vital new insights into mechanistic aspects of conversion-based reactions, including the role of electrolyte formulation and its influence on solution-mediated electrochemical processes,12–13 illumination of complex electrochemical-chemical conversion mechanisms,14–15 and substantial progress at the interface of electrochemistry and chemical physics of gas-to-solid conversion reactions including thermodynamics, kinetics, and transport considerations.16–21 Thus, it is worthwhile to continue pushing the limits and possible applications of metal-gas electrochemistry, especially Li-gas systems, by investigating new chemistries that offer equally or more attractive theoretical energy densities than the metal-O₂ systems. Such systems, even if not a priori rechargeable, can fill needed shorter-term gaps in technologies where higher energy density batteries are essential, such as for military, aerospace, and commercial use, while providing new understanding of electrochemical gas-to-solid transformations that appear poised to play an important role in future energy applications.
In considering prospective gas conversion cathodes with high energy density, it is first informative to compare the tradeoffs in voltage and capacity that distinguish today’s state-of-the-art, high-energy Li primary batteries from the “beyond Li-ion” batteries currently under development (Figure 1). Whereas Li-based primary batteries such as Li-MnO₂, Li-SO₂, and Li-SOCl₂ typically exhibit moderately high discharge potentials (~3-4 V vs. Li/Li⁺),²²-²⁵ capacities are limited to below ~500 mAh g⁻¹, arising from the high molecular weight of active compounds per unit charge stored. One notable exception is the Li-CFx solid-solid conversion battery based on carbon reduction and formation of solid LiF; the high capacity (865 mAh g⁻¹ theoretical) compensates for the somewhat lower voltages (~2.2 – 2.5 V vs. Li/Li⁺) that are attainable in practice.²⁶-²⁷ Continuing this trend towards moderate voltages but higher capacities are the “beyond Li-ion” systems such as the metal-O₂ and lithium-sulfur (Li-S) batteries²⁸ currently under widespread development. The high theoretical energy density of the Li-O₂ system, in particular, arises from the light weight of both reactants, yielding a high theoretical capacity (1168 mAh g⁻¹ Li₂O₂⁻¹) at a potential of 2.96 V vs. Li/Li⁺, with an overall gravimetric energy of 3557 Wh kg⁻¹ (based on the weight of Li₂O₂) (Figure 1). This is one of the highest theoretical energy densities to be realized among today’s batteries, in spite of the somewhat lower cell voltages, owing to the substantial gains in capacity possible from lightweight conversion reactions.
Figure 1. Theoretical voltages and cell capacities of Li primary batteries, metal-O\textsubscript{2} and Li-S batteries, and comparison with the Li-SF\textsubscript{6} system\textsuperscript{24-25}.

The aim of this current work was to examine whether parallel improvements in energy density are realizable with other gas cathodes by considering an alternative reaction mechanism than those of O\textsubscript{2}-based systems, namely, a high-capacity reduction reaction involving multi-electron transfer (n > 4) and full decomposition (by electron-coupled bond breaking) of a complex, multi-ligand gas. Such a reaction would be unparalleled among current gas cathode systems. To date, although a 4-electron transfer is theoretically possible in metal-gas systems based on O\textsubscript{2}, only 1-electron (for Na-O\textsubscript{2} and K-O\textsubscript{2})\textsuperscript{29-30} or 2-electron (Li-O\textsubscript{2})\textsuperscript{31} reactions are observed in practice. Interestingly, halogenated molecules with highly oxidized central atoms, e.g. sulfur or carbon, represent an alternative chemical family with the possibility to compete with or exceed the capacity of O\textsubscript{2}-based reactions: electron transfer can be accommodated by ligand abstraction and reaction with alkali metal cations, forming nLiX (n = number of ligands and X = F or Cl, for example).
Owing to the number and variety of halogenated molecules, a large reaction space is possible in which the capacity and potential can be tailored by tuning the reactant structure, including number and type of ligands. One important criterion is to identify systems in which the added weight of more complex halogenated molecules is compensated by large numbers of electrons transferred (for high capacity) and potentials competitive with today’s conversion-based systems, i.e., in the voltage range of 2 – 3 V vs. Li/Li⁺. In this work, we demonstrate the viability of such a “beyond-O₂” type gas cathode using a highly perfluorinated gas, sulfur hexafluoride (SF₆), as a model system to demonstrate the feasibility of such an approach. SF₆ contains sulfur in its highest oxidation state (S⁶⁺) and therefore offers the possibility of, at maximum, an 8-electron reduction, via the following reaction during discharge:

Anode: 8Li → 8Li⁺ + 8e⁻

Cathode: SF₆(g) + 8e⁻ + 8Li⁺ → 6LiF(s) + Li₂S(s)

yielding the overall cell reaction SF₆(g) + 8Li → 6LiF(s) + Li₂S(s) (ΔG°ₚ = - 2581 kJ mol⁻¹, E° = 3.69 V vs. Li/Li⁺). The combination of high potential and capacity (1063 mAh g⁻¹, based on the total weight of reactants) offers an exceptionally large theoretical gravimetric energy of 3925 Wh kg⁻¹. However, SF₆ is a classically inert compound, and the reaction between Li and SF₆ has heretofore only been known as a chemical reaction at temperature in excess of 800 °C. Although the electrochemical reaction of SF₆ with Mg has been conceptually proposed in a single earlier study, electrochemical reduction of SF₆ has never been conclusively demonstrated in practice.

We report here that the activity of SF₆ can be unlocked at a relatively simple carbon electrode and using a conventional glyme-based electrolyte, in a configuration that is similar to that of metal-O₂ batteries, and yields high capacity (in this study, up to ~3600 mAh g⁻¹ at 30 mA
g_{c^1}) at ~2.2 V vs. Li/Li^+. Through qualitative and quantitative analysis of the solid and liquid phases post-discharge, we determine the products formed, and establish that the theoretical 8-electron reaction can indeed be realized in practice. We also establish, using rotating-disk voltammetry, that the reduction reaction is limited by sluggish kinetics of the first electron transfer, followed by rapid subsequent reduction and full defluoridation of SF₆ reduction intermediates to form solid phases (predominantly LiF). This work demonstrates that high-capacity, multi-electron transfer reactions exceeding those reported previously can be harnessed successfully at non-catalyzed electrodes. In addition, we find that significant opportunities exist to tailor the electrode structure and electrolyte chemistry to modulate the discharge reaction and achieve improved capacities and discharge voltages.

EXPERIMENTAL SECTION

Chemicals and Materials. All solid chemicals, electrodes, and cell-making materials were dried prior to use and stored in an argon-filled glovebox (MBRAUN, H₂O < 0.3 ppm and O₂ < 15 ppm). Lithium perchlorate (LiClO₄, Sigma Aldrich, battery grade, 99.9% metal basis) was dried for 24 hours under active vacuum in a glass oven (Buchi) at 70 °C. Tetra ethylene glycol dimethyl ether (TEGDME, Sigma Aldrich > 99%), dimethyl sulfoxide (DMSO, Sigma Aldrich > 99.9%), propylene carbonate (PC, Sigma Aldrich > 99%), and acetonitrile (MeCN, Sigma Aldrich > 99%) were dried over fresh molecular sieves (Type 3 Å, Sigma Aldrich) that had been previously dried under active vacuum in a glass oven at 120 °C for at least 24 hours. The water content in the electrolyte was measured using a Karl Fisher titrator (Metler Toledo) and was found to be typically < 10 ppm.
**Carbon Electrode Fabrication.** Cathodes were prepared by coating sonicated inks composed of Vulcan carbon (VC, XC72, Cabot), Li-ion exchanged Nafion (LITHion™ Dispersion, Ion Power, Nafion/carbon wt. ratio of 1:2), and isopropanol onto a microporous separator film (Celgard 480, 25 µm thickness) or Toray carbon paper (TGP – H – 030, 110 µm Fuel Cell Store). The cathodes were then air-dried at room temperature and punched to 12 mm diameter, prior to drying in a glass oven under active vacuum at 70 °C for 24 hours. The typical thickness of the carbon layer on the electrodes was 15 µm for Celgard-coated electrodes, and the corresponding Vulcan carbon loading was $0.28 \pm 0.08 \text{ mg}_c \text{ cm}^{-2}$ or $0.37 \pm 0.07 \text{ mg}_c \text{ cm}^{-2}$ on Celgard separators or on Toray paper, respectively (error bar represents four measurements).

**Electrochemical Cell Assembly and Testing.** Two-electrode Swagelok electrochemical cells were constructed using a 10 mm diameter disk of Li metal as the negative electrode (0.38 mm thickness, Sigma Aldrich), which was pre-stabilized by soaking in 0.1 M LiClO$_4$ in PC for several days before use. The cells were assembled inside the glovebox using 0.3 M LiClO$_4$ in TEGDME as the electrolyte. Following assembly, the cells were purged with SF$_6$ (Airgas, 99.999% purity) within the glovebox for approximately 5 minutes, were pressurized to ~1.5-1.8 bar, and were sealed for subsequent measurement outside the glovebox. The Li – SF$_6$ cells were rested at open circuit voltage (~ 2.7 – 2.9 V vs. Li/Li$^+$) for 15 hours, before being galvanostatically discharged (Biologic VMP3 or MPG2 Workstation) at specified currents to a voltage cutoff of 1.6 V vs. Li/Li$^+$.

**In Situ Pressure Monitoring.** The pressure – coupled measurement was conducted using a pressure transducer (PX309, Omega) fitted to a modified Swagelok design. The cell was discharged inside an incubator at 25 ± 1 °C.
**Rotating Disk Electrode Measurements.** Three-electrode electrochemical measurements, conducted within an Ar glovebox, employed a glassy carbon disk (GC, Pine, 0.196 cm$^2$) as the working electrode, a Ag wire immersed in 0.01 M AgNO$_3$ and 0.1 M TBAClO$_4$ in MeCN (housed within a fritted glass tube) as the reference electrode, and Pt wire contained within a fritted glass compartment and filled with the working electrolyte as the counter electrode. Prior to each set of scans, the GC electrode was polished using de-ionized water (18.2 MΩ cm, Millipore) in the following sequence: 5 µm, 3 µm, 1 µm, and 0.3 µm polishing papers (Thor Labs) until a mirror finish was obtained, followed by sonication in DI water for 5 minutes and drying under active vacuum in a glass oven (Buchi) at 70 ºC for at least 12 hours. Finally, electrodes were transferred directly into the glovebox without exposure to the ambient.

To establish the potential of the reference electrode relative to Li/Li$^+$, a piece of Li metal was first placed in the electrolyte solution (without SF$_6$) and its potential was monitored vs. Ag/Ag$^+$ until stabilization (approximately 30 minutes), at which point the potential difference was measured: $0 \text{ V}_{\text{Li}} = -3.47 \text{ V vs. Ag/Ag}^+$ in 0.3 M LiClO$_4$ in TEGDME. Following determination of the Li/Li$^+$ potential, the working electrode was then immersed in the electrolyte and steady state CVs were obtained under a passive argon headspace by scanning the GC electrode potential from 1 – 3 V vs. Li/Li$^+$ at a scan rate of 20 mV s$^{-1}$. Next, SF$_6$ was bubbled into the electrolyte for 10 minutes prior to the CV measurements.

**Solid Phase Characterization.** SEM was conducted on discharged cathodes using a Zeiss Merlin high-resolution SEM operating at an accelerating voltage ranging from 2 kV to 5 kV and beam current of 100 pA. XRD was obtained on both the pristine and solvent-rinsed discharged electrodes using a PANalytical X'Pert Pro with a copper anode (Cu K$\alpha$). An air-sensitive sample holder was
used to seal the discharged electrode to minimize atmospheric contamination during measurements. All scans for LiF detection were performed from $30^\circ < 2\theta < 90^\circ$ at a typical scan speed of $0.3^\circ \text{min}^{-1}$. XPS measurements were performed on discharged cathodes using a non-monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source which was at $54.7^\circ$ relative to analyzer axis and operated at 400 W (15 kV and 27 mA). The chamber was operated at $\sim 2 \times 10^{-8}$ mTorr vacuum and the electron takeoff angle was 45°. The S2p spectra peaks were fitted using equal full width half maximum doublets with an area ratio of 2:1 and spin splitting of 1.18 eV. The charging effects were compensated by calibrating all spectra with the F1s peak for the LiF to 685.0 eV.

**Spectroscopic Measurements.** UV-vis measurements were performed on an Agilent Cary 60 UV-vis Spectrometer. $^{19}$F NMR and $^1$H NMR measurements were performed using a Varian Mercury 300 MHz NMR spectrometer equipped with a 5 mm PFG (pulsed field gradient) quad probe. Electrolytes were purged with SF$_6$ for ten minutes in a closed glass cell and rested for two hours. For sample preparation, 600 µL of the electrolyte along with 120 µL of DMSO-d$_6$ (Sigma Aldrich, used for locking) was introduced into a capped Wilmad NMR tube (528-PP-7) for $^{19}$F NMR analysis. $^1$H NMR was performed on antechamber-dried electrodes washed in D$_2$O (Sigma Aldrich, > 99.9%). Quantification of LiF in discharged electrodes was also performed with $^{19}$F NMR by introducing a known internal standard of 2,2,2–trifluoroethanol (TFE, Sigma Aldrich > 99.5%). The amount of LiF present in galvanostatically discharged cathodes was determined using the following procedure: Discharged cathodes were dried, without rinsing, inside the antechamber of the glovebox for approximately one hour or until all of the solvent evaporated, and were then soaked in known amounts of D$_2$O to dissolve the solid LiF. A portion of this solution was then extracted and transferred to an NMR tube, into which a known amount (5.5-13.7 mM) of 2,2,2–trifluoroethanol (TFE, Sigma Aldrich > 99.5%) was added as an internal standard. The validity of
TFE as an internal standard was confirmed separately by measuring the relative integrated areas $I_{\text{TFE}}/I_{\text{LiF}}$, and comparing to the theoretical ratios by varying different concentrations of LiF (0 ~ 35 mM) and dissolving 13.7 mM of TFE. The LiF peak was observed at -122 ppm with the D$_2$O cathode wash, which is in good agreement with previous observations.$^{37-38}$

RESULTS AND DISCUSSION

As a complex, multi-electron transfer reaction can involve multiple pathways, we begin by briefly considering the reactions possible upon electrochemical reduction of SF$_6$ in the presence of Li$^+$ ions. SF$_6$ is described in the literature as a highly stable, nonreactive gas,$^{39-40}$ and therefore, relatively little remained known about its room-temperature reaction chemistry until fairly recently.$^{41-45}$ Owing to its octahedrally-coordinated shell of highly electronegative fluoride ligands, SF$_6$ is nonpolar, and exhibits high dielectric strength and electron-capture ability that make it a good dielectric insulator. Its spark breakdown under high electric fields, and subsequent gas-phase decomposition products, have been studied in this context,$^{46}$ and help to inform our own analysis in considering accessible electrochemical reduction pathways. Among the possible lower fluorides of SF$_6$, two – sulfur tetrafluoride (SF$_4$) and disulfur decafluoride (S$_2$F$_{10}$) – are stable and isolable in the gas phase. However, thermochemical properties of nearly all the lower fluorides (SF$_x$, 1 ≤ x ≤ 6) are readily accessible in thermochemical databases. This has enabled us to predict theoretical electrochemical potentials based on reaction thermodynamics. As shown in Table S1 and Figure 2, multiple pathways are possible in competition with that of the nominal 8-electron transfer reaction listed previously, with the most feasible being the 6-electron transfer reaction (forming S + 6LiF, $E^o = 4.18$ V vs. Li/Li$^+$), the 2-electron transfer reaction (forming SF$_4$ + 2LiF, $E^o = 4.06$ V vs. Li/Li$^+$), two 1-electron transfer reactions and dimerization of SF$_5$ (forming S$_2$F$_{10}$ + 2 LiF, $E^o = 3.22$ V vs. Li/Li$^+$, not depicted), or a series of sequential 1-electron transfer reactions. It is worth
noting that the 2, 6, and 8-electron transfer reactions have thermodynamic potentials that are higher than, or overlap with, those of sequential 1-electron reactions. Therefore, a significant aspect of this work is devoted to untangling the actual reaction stoichiometry occurring in practice, because electrochemical potentials may not uniquely reveal the reaction taking place.

**Figure 2.** Schematic representation of thermodynamic redox potentials of different SF\textsubscript{6} conversion pathways: 8-, 6-, and 2-electron concerted processes (orange, purple, and blue traces, respectively) and the sequential 1-electron transfer pathway (red). Equivalents of LiF formed at each step are not explicitly noted for clarity (refer to Table S1 for balanced reactions).
**SF₆ Solubility and Chemical Stability in Li-Based Cells**

Prior to conducting electrochemical measurements, it was first necessary to evaluate the chemical compatibility of SF₆ with the electrolyte and determine its solubility. We selected a standard glyme, tetraethyleneglycol dimethyl ether (TEGDME), as the electrolyte for this initial study owing to its low vapor pressure and relatively good stability with both Li and in the presence of strong Lewis bases such as O₂ (anticipating that F⁻ could potentially be generated as an intermediate upon SF₆ reduction). The electrolyte salt, 0.3 M LiClO₄, was chosen to avoid additional sources of fluorine that could overlap with quantitative analysis of reduced SF₆ products, as presented later in the text. Upon bubbling SF₆ into TEGDME electrolyte, ¹⁹F NMR measurements confirmed that SF₆ remained fully intact, as evidenced by a single peak at 59 ppm in good agreement with gas-phase ¹⁹F NMR measurements of SF₆ (Figure S1). The dissolved SF₆ was stable in the electrolyte over timescales of at least ~1 week. The solubility of SF₆ in TEGDME electrolyte (Figure 3) was measured, using a home-built apparatus (Figure S2), to be ~2-3 mM in TEGDME electrolyte at a typical cell headspace pressure of ~1.6 bar. Although the solubility of nonpolar SF₆ is fairly low in polar TEGDME electrolyte compared to its reported solubility in nonpolar solvents (~10 – 60 mM), its solubility is comparable to that of O₂ in typical metal-O₂ battery electrolytes (approximately 1-10 mM). It is worth noting, given the large size of SF₆, that relative expected differences in diffusivity, as determined from the Stokes equation (Figure S3) can be estimated by comparing the hard-sphere radius of SF₆ (approximately 1.6 Å) to that of O₂ (1.2 Å, based on the O-O bond distance) which predicts a diffusion coefficient fractionally lower than O₂ in a given electrolyte (e.g., D₆SF ~ 3.4 x 10⁻⁶ cm² s⁻¹ in TEGDME vs. D₂O₂ ~ 4.5 x 10⁻⁶ cm² s⁻¹). Therefore, at first pass, the larger molecular size and transport behavior are not expected to impart a substantial penalty to the diffusion of SF₆. However, to verify whether transport
limitations influenced the electrochemistry over typical currents explored in this work, we conducted hydrodynamic voltammetry measurements, as described later in the text.

Figure 3. a) Typical dynamic pressure-decay response after purging SF$_6$ into the evacuated headspace of the pressure cell apparatus. b) Saturation concentration of dissolved SF$_6$ as a function of the partial pressure, $p-p_o$, of SF$_6$ introduced in the solubility apparatus headspace. $p_o$ indicates the nominal vacuum pressure of residual argon prior to introducing the SF$_6$ (typically ~0.1 bar).

As Li is known to chemically react with SF$_6$ at high temperatures,$^{33-34}$ we also examined the chemical reactivity of SF$_6$ with dry and with electrolyte-immersed Li foils at room temperatures. Any reactivity must be suppressed to avoid parasitic consumption of the reactant gas and lowering of the cell thermodynamic efficiency and voltage during discharge. As shown in Figure S4a, Li metal foils that were rolled and exposed to an SF$_6$ gas environment indeed discolored slowly, over the course of approximately one day. This reactivity could be suppressed by pre-soaking rolled Li electrodes in 0.1 M LiClO$_4$ (propylene carbonate) electrolyte for several days to grow a pre-formed Solid Electrolyte Interphase (SEI) passivation layer prior to cell assembly.$^{36}$ Subsequent three-electrode measurements (Figure S4b) indicated that the open circuit
potential of the pre-passivated Li remained stable upon immersion in SF$_6$-saturated electrolytes, within +/- 2 mV over 24 hours, which was also equal to that obtained in standard 0.3 M LiClO$_4$ (TEGDME) electrolyte without SF$_6$ (0 V vs. Li/Li$^+$ = -3.466 V vs. Ag/Ag$^+$). All stabilized Li electrodes were consistently found to retain their metallic finish throughout the duration of cell measurements, even after long-term discharge for several weeks (Figure S4c).

**Galvanostatic Discharge and Rate Capability**

The electrochemical activity of the Li-SF$_6$ system was examined in a prototype metal-gas battery built within a modified Swagelok electrochemical cell (Figure S5). The cell consisted of a pre-passivated Li anode, a carbon (Vulcan XC72) cathode coated onto a porous Celgard separator, and the electrolyte, 0.3 M LiClO$_4$ in TEGDME, into which SF$_6$ was solubilized by purging the cell headspace and pressurizing it to ~1.6 bar. Galvanostatic discharge measurements were conducted from open circuit (typically ~2.7 – 2.9 V vs. Li/Li$^+$) to a lower voltage cutoff of 1.6 V vs. Li/Li$^+$. As seen in Figure 4a, galvanostatic discharge resulted in a well-defined plateau, which was absent without the SF$_6$ present (Figure S6). At the lowest rate examined (7.5 mA g$_C^{-1}$), the discharge potential with SF$_6$ was approximately 2.25 V vs. Li/Li$^+$, and discharge proceeded to high capacities of 3844 mAh g$_C^{-1}$ before the voltage rapidly decreased. Increasing the discharge current resulted in a gradual lowering of the discharge capacity and potential, e.g., 1083 mAh g$_C^{-1}$ was obtained at a discharge current of 150 mA g$_C^{-1}$, with an average voltage of ~1.9 V vs. Li/Li$^+$. The lower capacities attainable with higher rates were found to result largely from rate limitations in non-optimized, thin (15 μm) Vulcan carbon cathodes coated on non-conductive Celgard separator, as evidenced by the fact that similarly-prepared Vulcan carbon cathodes coated onto a conductive substrate (Toray carbon paper) exhibited improved rate capabilities, yielding capacities up to ~1750 mAh...
\( g_c \) at an average potential of 1.70 V vs. Li/Li\(^+\) at 1000 mA \( g_c \) (Figure 4b). Impedance measurements of the two electrode preparations supported the fact that Celgard-coated separators had significantly higher DC resistance (133 Ω vs. 40 Ω on Celgard – coated separators vs. Toray – loaded VC electrodes, respectively, Figure S7). Therefore, improved rate capabilities appear feasible with the SF\(_6\) system. We note that the specific capacity of electrodes will depend not only on conductivity but also sensitively on the electrode porosity, which determines the amount of solid phases that can accumulate during discharge. Future studies will be conducted to develop optimized electrode architectures for higher rates. In the remaining text, characterization was conducted on Celgard-coated VC electrodes for simplicity unless explicitly noted.

Interestingly, the highest attainable potential in TEGDME (~2.25 V vs. Li/Li\(^+\)) is lower than that of any of the thermodynamically predicted pathways (Figure 2, Table S1), in some cases by more than 1 V, and thus the reduction potential cannot alone be used to extract meaningful information about the discharge reaction. Therefore, we next performed a series of qualitative and quantitative analyses to evaluate the reaction taking place.
Figure 4. a) Galvanostatic discharge profiles on Vulcan carbon electrodes coated onto Celgard separators, with capacity normalized to the weight of carbon, in Li – SF₆ cells at various current densities with a lower voltage cutoff of 1.6 V vs. Li/Li⁺. B) Rate capability of Vulcan carbon cathodes coated onto Toray paper and discharged to higher rates (up to 1000 mA g⁻¹). C) In situ pressure monitoring during discharge at 150 mA g⁻¹ for separator-supported cathodes, and the corresponding Coulombic ratio calculated using the ideal gas law in the cell headspace.
Determination of Discharge Products and Reaction

The reaction stoichiometry underlying the galvanostatic behavior in Figure 4 was determined using a combination of gas-, solid-, and liquid phase analyses. First, the participation of the gas phase in the observed electrochemical reaction was confirmed by monitoring the cell headspace pressure during discharge. As shown in Figure 4c, for a representative cell discharged at a typical current of 150 mA g\(^{-1}\), the pressure was found to decrease linearly upon initiation of the reduction current, and the gas consumption rate remained constant throughout discharge at a Coulombic ratio close to that of \(~8\) e/molecule. Moreover, similar results were obtained for cells discharged at 75 mA g\(^{-1}\) (Figure S8), which yielded an average of \(8.44 \pm 0.41\) e/molecule (based on 3 measurements). A Coulombic ratio close to 8 e/molecule permits identification of the majority reaction as that forming six equivalents of LiF (one for each fluoride ligand) and one equivalent of Li\(_2\)S per molecule of SF\(_6\). These pressure measurements clearly indicate that incomplete reduction to elemental sulfur is not the primary reaction (i.e., \(6\) e/molecule was not observed), nor is the formation of the gas S\(_2\)F\(_{10}\) (2 e/molecule; an average of the 8-electron reaction and any of the above two reactions would yield less than 8 e/molecule, which was also not observed). \(^1\)H NMR analysis of electrolyte extracted from discharged cells revealed that no observable solvent degradation occurred during discharge (Figure S9), which indicates that the additional Coulombs passed during discharge were not related to direct parasitic electrolyte reactions. Therefore, the slight but statistically significant excess in number of electrons above 8 e/molecule leads us to conclude that some quantity of the gas SF\(_4\) may be formed as a minor side product (we note that majority formation of SF\(_4\) can be ruled out, as it would correspond to a 1-to-1 conversion between two gases and would result in no decrease in headspace pressure).
Unfortunately, SF₄ has similar fragmentation patterns as the parent SF₆, which prevents its direct confirmation by mass spectroscopy.

To determine the composition of reduction products, discharged cathodes were extracted from terminated cells for solid phase analysis. As shown in Figure 5a, SEM images of discharged cathodes revealed the formation of visible solid products, which grew as a homogeneous coating on the Vulcan carbon particles, as evidenced by an increase in the average particle size from approximately <50 nm to ~150 nm in diameter following discharge. X-ray diffraction of discharged cathodes (Figure 5b) confirmed that LiF was present as the only crystalline product (LiF: Space Group: F m̅3 m, JCPDS: 00-004-0857), i.e., no crystalline sulfur phases were evident. The amount of LiF formed during discharge was quantified by ¹⁹F NMR measurements of D₂O-extracted discharged cathodes following a previously reported method³⁷ and indicated that, within measurement error, 6/8 of the discharge capacity was fully accounted for by detected LiF (i.e., 29.55 ± 3.96 µmol LiF mAh⁻¹ were formed across 5 measurements, compared to a theoretical value of 27.98 µmol LiF mAh⁻¹, Figure S10), in good agreement with the proposed stoichiometry.
**Figure 5.** a) SEM images of cathodes fully discharged to 1.6 V vs. Li/Li⁺ at 75 mA g⁻¹ (capacity = 1641 mAh g⁻¹). A pristine cathode is shown in the inset of (a) for comparison. Both scale bars are 200 nm. b) XRD pattern of a pristine and fully discharged cathode at 75 mA g⁻¹ (capacity = 1100 mAh g⁻¹). The Miller indices of LiF are referenced to JCPDS: 00-004-0857.

Having established that the fluoride ligands of SF₆ are converted into solid LiF with high Coulombic efficiency during reduction, we next turn to determining the fate of sulfur using X-ray photoelectron spectroscopy (XPS) of discharged cathodes. Owing to the surface sensitivity of XPS (~10 nm) and the thicker (~ 50 - 100 nm) solid phase deposits, measurements were conducted at several depths using argon sputtering. At the very surface layers, the S2p spectra of a typical discharged electrode (Figure 6a) revealed a peak at 161.8 eV, indicative of Li₂S₂, and a peak at 163.7 eV, indicative of S₈ (reference spectra for S₈ and Li₂S are provided in Figure S11). In addition, two sets of doublets at higher binding energy (approximately 166 – 171 eV) were attributed to highly oxidized sulfur such as sulfate or polythionate species. The sulfate peak at 166.4 eV arises in part from the Nafion binder, whereas the higher-binding energy peaks could be attributed to oxidation of the very surface layers of discharged cathodes during transfer to the vacuum chamber. To verify this, and to probe the composition of sulfur products below the immediate surface layer, depth profiling was performed at two additional depths (Figure 6b-c). As shown in the corresponding F 1s spectra (Figure 6d-f; corresponding C 1s spectra are included in Figure S12), a single peak corresponding to LiF at 685.0 eV was present in all spectra and remained unchanged with increasing depth. In contrast, significant changes were observed in the S 2p spectra. First, the relative amounts of oxidized sulfur decreased significantly, consistent with the removal of surface-localized contamination. In addition, reduced sulfur corresponding to Li₂S (~160.0 eV) was revealed. Higher-order polysulfide species (~163 eV) were also observed,
however, little elemental sulfur was found beyond the near-surface layers. These results are interesting, because they indicate a more complex sulfur speciation than that suggested by the pressure-based reaction stoichiometry alone, which suggests only Li$_2$S as the discharge product. We address this further in the following section. Importantly, integration of the peak areas corresponding to reduced sulfur species (152 – 172 eV and 678 – 692 eV for S 2p and F1s region, respectively) compared to the area of LiF in the F 1s spectra indicated that the overall amount of sulfur products remaining in the electrode was significantly less than that expected based on the reaction stoichiometry, i.e. S:F ratios of roughly ~ 1:30 were observed at all depths, compared to an expected ratio of 1:6.

**Figure 6.** High resolution XPS spectra of a fully discharged cathode (capacity = 1290 mAh g$^{-1}$) at 75 mA g$^{-1}$ in 0.3 M LiClO$_4$ in TEGDME. a-c) S 2p high-resolution spectra at 0, 180, and 720 s of sputtering; d-f) corresponding F 1s spectra.
The above observations, in particular a lower-than-expected quantity of sulfur products in the discharged electrode and the presence of some polysulfides, strongly point towards a solution-based process occurring in the electrolyte during discharge. Polysulfides are known to be moderately soluble in glyme electrolytes. However, polysulfides are challenging to detect in our typical discharged cells because of the low concentrations and/or relatively small volume of extractable electrolyte following discharge. Therefore, to evaluate whether soluble species were indeed generated by SF₆ reduction, we conducted a discharge experiment using the higher-capacity Toray – loaded VC electrodes used previously (Figure 4b) in order to increase the concentration of formed soluble species. Indeed, the extracted cathode from Toray-VC electrodes (~ 3500 mAh g⁻¹) exhibited a bright emerald green color (Figure 7a-b) which was not easily observable with lower capacities (1500 mAh g⁻¹). Moreover, the washed solution exhibited absorption in the UV-visible spectrum around 350, 470 and 617 nm, characteristic of higher-order polysulfides, specifically, S₆²⁻ in TEGDME (Figure 7c-d). Taken together, these data provide strong evidence that once the SF₆ is defluorinated, the subsequent electrochemistry converts largely into a discharge reaction based on sulfur electrochemistry. To synthesize the observations from various measurement techniques, we next discuss the proposed reduction mechanism below.
Figure 7. a) Image of fully discharged separator. b) Image of solution extracted from rinsing fully discharged separator and cathode (capacity = 3646 mAh g\textsuperscript{-1} at 75 mA g\textsuperscript{-1}) in TEGDME. c) Image of 2.5 mM Li\textsubscript{2}S\textsubscript{6} in TEGDME for visual comparison. d) UV-vis spectrum of the solution in (b).

Discharge Reaction and Proposed Mechanism

While pressure measurements suggest a Coulombic ratio close to 8 e/molecule, the modestly higher value observed on average (ranging between ~8.0 – 8.9 e/molecule across several measurements) is critical to understanding the range of products formed during discharge. Such a number is broadly consistent with the nominal 8-electron reaction, SF\textsubscript{6} + 8Li → 6LiF + Li\textsubscript{2}S, however, would also be consistent with the formation of relatively small amounts of SF\textsubscript{4}, as described previously. Recalling that the measured Coulombic ratio is only an average and could
reflect multiple possible branching reactions, this number also does not exclude the formation of moderate quantities of sulfur (6 e/molecule), as long as the final numbers average to slightly higher than 8. This picture is consistent with the observation of elemental sulfur at the surface layer of discharged cathodes from XPS measurements (Figure 6a). We emphasize, however, that Li$_2$S is still the majority discharge product that is consistent with both the in situ pressure measurements as well as the LiF quantification. The presence of Li$_2$S in discharged electrodes from XPS measurements provides evidence that the full reduction of SF$_6$ is possible, and should be thermodynamically favored as long as there is sufficient surface area to complete the full 8-electron reduction. It is also important to note that SF$_4$ and S$_2$F$_{10}$ species are expected to be much more electrochemically active than SF$_6$ once formed (Table S1) due to both thermodynamic and steric (kinetics) considerations, and thus, are likely to continue to react provided they have sufficient contact with the electrode surface.

The lower-than-expected quantity of Li$_2$S found within discharged cathodes can be rationalized by the relatively low formation rates of reduced sulfur species, as well as known solubility and reactivity of reduced sulfur phases in glyme electrolytes. Li$_2$S, formed at atomistic scales (i.e., as an S$^2^-$ anion) in molecular SF$_6$ conversion (in contrast to bulk-phase solid conversions in conventional Li-S batteries) exhibits small but finite solubility in glyme electrolytes (reportedly $\sim$1 mM).$^{52}$ Typical discharge rates of 75 mA g$^{-1}$ used in this study would correspond to an estimated rate of S$^3^-$ formation of $\sim 3 \times 10^{-11}$ mol$_{sulfide}$ s$^{-1}$, which would lead to concentrations of approximately 1.4 mM in the electrolyte after one hour of discharge (based on an electrolyte volume of 75 $\mu$L). Therefore, loss of Li$_2$S by solubilization is feasible. In addition, once Li$_2$S (solid or solubilized) and/or elemental sulfur is present in the electrode or electrolyte, chemical reactions can occur to generate soluble polysulfides, as occur typically in Li-S batteries.$^{54}$ Based on visual
comparison with prepared standards in our lab, the concentration of sulfur extracted from high-capacity electrodes in Figure 7 was estimated to be approximately 10 mM; from arguments above, this can reasonably be formed within cells over the timescale of several hours (based on calculations at 75 mA g\text{c}^{-1}). The subsequent chemical and/or electrochemical reactions are likely highly complex, and understanding the detailed mechanisms and fate of polysulfides, once present, are beyond the scope of the current work. Future studies will be dedicated to this rather unusual mechanism of polysulfide generation, which is distinct from that occurring in more conventional Li-S batteries.

**Kinetic and Transport Behaviors Determined from Cyclic Voltammetry**

With the overall discharge reaction established, it is possible to meaningfully compare the observed reduction potentials to the theoretical value for either the concerted 8-electron pathway (3.69 V vs. Li/Li\textsuperscript{+}), or the sequential reduction pathways shown in Figure 2. Although it is not possible to know the detailed reduction mechanism (i.e., concerted vs. sequential 8-electron transfer) at this stage, clearly, the observed potentials attainable on discharge are significantly lower than the potentials of any of the above reactions, which indicates that a significant overpotential (1 V or greater) is required for SF\textsubscript{6} reduction. To elucidate the nature of this overpotential, cyclic voltammetry measurements were conducted using a rotating disk electrode (RDE) setup employing planar glassy carbon (GC; A = 0.196 cm\textsuperscript{2}) electrodes. Although the discharge regimes explored using planar GC electrodes and high surface area VC electrodes are not perfectly comparable owing to differences in surface areas, RDE is an indispensable tool for distinguishing kinetic and transport phenomena intrinsic to electrochemical reactions. We use it here to glean essential insights into the nature of the rate-limiting step in SF\textsubscript{6} reduction.
As shown in Figure S13a, reduction of \( \text{SF}_6 \) under quiescent (non-rotating) conditions exhibited an onset potential around \( \sim 1.77 \) V vs. \( \text{Li/Li}^+ \), evaluated at a current density of \( 50 \mu \text{A cm}^{-2} \). This is slightly lower than reduction potentials observed in two-electrode measurements, likely resulting from the lower surface area of GC electrodes. A large peak current was reached during the negative scan at \( \sim 1.4 \) V vs. \( \text{Li/Li}^+ \), and the current then rapidly decreased. No oxidation current was observed on the positive-going scan. We note that this was also consistent with galvanostatic attempts to recharge the battery, which yielded negligible capacity (Figure S14). The non-rechargeability can be attributed to the electronically insulating nature of LiF and/or sulfur phases present in the discharged electrode, as well as the intrinsically high irreversibility of \( \text{SF}_6 \) reduction and conversion, which effectively deconstructs \( \text{SF}_6 \) into its constituents and results in physically separated solid phases. Interestingly, even upon rotation up to 900 rpm (Figure S13b), no significant changes were observed in the CV profiles. This indicates that, first, kinetic, rather than transport limitations, dominate the rising wave of the reduction scan, and are therefore responsible for the large observed overpotentials. This is expected from the high inertness and poor polarizability of \( \text{SF}_6 \), which arises from its octahedral symmetry. It is reasonable to hypothesize that the high overpotentials originate from weak attraction and interactions of \( \text{SF}_6 \) with the carbon surface, and/or to intrinsically slow kinetics of S-F bond breaking, both of which could give rise to sluggish electron transfer. The CV results show that even highly convective conditions do not modify the reaction rate at any potential during the reduction scan.

Together, these findings suggest that the rate-limiting step of \( \text{SF}_6 \) reduction corresponds to the initial electron transfer, followed by a rapidly downhill reaction of reduced sulfur intermediates to form solid phases. Lower sulfur fluorides have high thermodynamic reduction potentials \( (E > 3.0 \) V vs. \( \text{Li/Li}^+) \), as shown in Figure S1, and are expected by steric arguments to have more facile
reduction kinetics than the nonpolar, highly inert SF$_6$. Thus, lower fluorides are expected to undergo facile reduction at reducing electrode potentials required to activate SF$_6$. The rapid subsequent electrochemical steps are supported by the fact that no additional reduction waves are observed at lower potentials, even at a lower scan rate of 5 mV s$^{-1}$ (Figure S15), and thus there is no evidence of sluggish kinetics (reflected by comparable or even higher overpotentials) for reduced sulfur intermediates. The rate-limiting first electron transfer step is also supported by the completeness of the reaction once SF$_6$ becomes activated, as well as the lack of substantial accumulation of intermediate products such as lower fluorides of sulfur, which would be expected if these subsequent reduction steps were instead rate-limiting. The nature of SF$_6$ reduction presents a challenge to characterize the stepwise reaction mechanism of SF$_6$ reduction, as the intermediates are likely extremely short-lived and not easily detectable.

With continued scanning to lower potentials, the rapid decrease in current is attributable to a fast passivation of the GC surface owing to LiF and/or insulating sulfur phase buildup at highly reducing potentials. This is in agreement with the lack of a limiting current even at 900 rpm, which suggests that soluble species, such as lone fluoride anions or reduced sulfur fluorides, are not formed in significant quantities under the conditions explored in CV measurements. It is worth noting that the second reductive scan (Figure S15b) yielded no additional current, confirming that the decrease in current following the reduction peak in the first scan corresponded to rapid passivation. These findings suggest that future efforts to improve solubility of LiF through electrolyte design, or control its morphology or spatial formation within architected electrodes with improved porosity, could be a promising strategy to further improve the capacity and rate capability of Li-SF$_6$ batteries.
Extension to Non-Glyme Electrolytes

Finally, to test whether the results herein are specific to glyme electrolytes, or whether SF$_6$ reduction is possible in other electrolyte systems, we also conducted parallel galvanostatic discharge measurements in 0.3 M LiClO$_4$ in dimethyl sulfoxide (DMSO), an electrolyte solvent that is highly relevant to metal-gas batteries.$^{1,36}$ As shown in Figure 8, the galvanostatic discharge of SF$_6$ in DMSO was qualitatively similar as in TEGDME, yielding a similar plateau and rapid decline at the end of discharge (negligible capacity was observed under an argon headspace, Figure S16). However, interestingly, both the discharge potential and the observed capacities were significantly higher in DMSO than in TEGDME. For instance, discharge at 30 mA g$^{-1}$ in DMSO yielded capacities of almost ~7800 mAh g$^{-1}$ at an average potential of ~2.5 V vs. Li/Li$^+$, whereas that in TEGDME was ~3600 mAh g$^{-1}$ at an average potential of ~2.2 V vs. Li/Li$^+$. SEM images revealed more sharply cubic deposits of LiF (Figure 8b) than in TEGDME, which were confirmed crystalline by XRD measurements (Figure 8c). This suggests a significant role of the electrolyte solvent in influencing the LiF precipitation and growth mechanism, and may help to rationalize the higher observed capacities in DMSO. As with TEGDME, significant coloration could be observed in extracted electrolytes following discharge, however, the solution was blue in DMSO, and UV-Visible measurements suggested a high preponderance of the shorter-chain S$_5^-$ radical (Figure 8d), which is known to be highly stable in DMSO.$^{55}$ Overall, future detailed measurements are needed to better understand how the role of solvent influences the complex reduction pathways and speciation of SF$_6$ and sulfur products, and an in-depth mechanistic study of SF$_6$ reduction in DMSO and other electrolytes will be the subject of future work. However, these results serve to indicate that, promisingly, the electrolyte solvent, in addition to the electrode architecture as demonstrated previously, can be an important parameter to tailor the electrochemical reactions in
Li-SF₆ batteries, and particularly those involving the derived sulfur phases. Although the SF₆ system currently exhibits significant overpotentials, it appears that significant improvements may be possible.

Figure 8. a) Galvanostatic discharge profiles on Vulcan carbon electrodes coated onto Celgard separators using 0.3 M LiClO₄ in DMSO electrolyte in Li – SF₆ cells at various current densities with a lower voltage cutoff of 1.6 V vs. Li/Li⁺. b) SEM images of cathodes fully discharged to 1.6 V vs. Li/Li⁺ at 75 mA g⁻¹ (capacity = 2466 mAh g⁻¹). c) XRD pattern of a fully discharged cathode at 75 mA g⁻¹ (capacity = 2466 mAh g⁻¹). The Miller indices of LiF are referenced to JCPDS: 00-004-0857. d) UV-vis spectrum of DMSO solvent used to rinse fully discharged separator.
CONCLUSIONS

We have presented an electrochemical gas-to-solid conversion reaction with high capacity based on the 8-electron electrochemical reaction of SF₆ with Li to form LiF and Li₂S. We demonstrated, first, that such a highly-fluorinated molecule, which has widely been regarded as inert, can be electrochemically activated at an electrified interface consisting of a simple carbon electrode and a conventional glyme-based electrolyte. Once activated, SF₆ and its reduction intermediates readily continue to accept electrons, leading to eventual total de-fluoridation and stoichiometric formation of LiF crystalline solids. Li₂S-Li₃S₂ solids and soluble intermediates are found within the cathode and electrolyte, indicating that the cell electrochemistry converts largely to that of a sulfur electrochemical system in the final reduction steps. Using a combination of in situ pressure monitoring, quantitative NMR, and spectroscopic analysis including XPS of extracted cathodes and UV-visible spectroscopy of extracted electrolytes, we also presented a platform to interrogate and comprehend a complex, multi-electron reaction through extensive analysis of products spanning liquid, solid, and gas phases. The high capacities (up to ~8000 mAh/g) reached in this work indicate the potential of alternative-gas cathodes to compete with the champion O₂-based gas cathodes, at least in terms of discharge capacity, although the SF₆ system is not rechargeable. The long-term viability of the Li-SF₆ system will depend on future efforts to improve the discharge voltage and kinetics. Continued fundamental studies into the origin of large overpotentials, potential strategies to catalyze the reduction kinetics, and detailed mechanistic study of the multi-electron transfer mechanisms will prove valuable. Overall, these results stress the significant opportunities that exist to continue exploring metal-gas electrochemical systems that capitalize on novel electrochemical conversion mechanisms beyond that of O₂.
ASSOCIATED CONTENT

**Supporting Information.** Table of SF₆ reduction pathways, measurements on gas solubility of electrolyte, calculation of diffusion coefficient, measurements on stability of Li anode, argon discharge in TEGDME, impedance spectra, additional electrochemical plots and material characterization figures.

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**Notes**

The authors declare no competing financial interest.

ACKNOWLEDGMENT

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TOC Graphic
Supplemental Information

A Lithium-Gas Battery Based on High-Capacity Sulfur Fluoride Conversion

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**SF$_6$ reduction pathways**

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**Sequential, 1-electron pathways**

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**Reduction reactions of possible gas intermediates, SF$_4$ and S$_2$F$_{10}$**

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<td>-4897</td>
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**Table S1.** Thermodynamic Gibbs Free Energy of reaction, and computed electrochemical redox potentials, of different SF$_6$ conversion pathways. Top table: Possible reactions starting with SF$_6$ and resulting in different final products (S, Li$_3$S, SF$_4$, or S$_2$F$_{10}$ with equivalents of LiF). Middle table: Stepwise 1-electron sequential reduction of SF$_6$. Bottom table: Reduction potentials of the most likely gas intermediates, SF$_4$ and S$_2$F$_{10}$. Thermochemical properties were obtained from the NIST Chemistry WebBook, SRD Number 69.
Figure S1. $^{19}$F NMR spectra of SF$_6$ purged into 0.3 M LiClO$_4$ in TEGDME after five days.

Figure S2. Apparatus used for solubility measurements based on a modified design reported elsewhere.$^1$ After loading the electrolyte (~9 mL) under an Ar environment, the pressure measurement cell was exposed to active vacuum until the pressure decreased to ~0.1 bar (denoted as $p_0$ in Figure S5 and recorded for each measurement), after which 1) the cell was rapidly pressurized with SF$_6$ via a three-way valve until the target initial pressure $p$ was reached, corresponding to a net pressure $p-p_0$ of SF$_6$ in the headspace; and 2) the cell was sealed by switching the valve to the ‘closed’ position. All measurements were conducted in an incubator maintained at 25 ± 0.1 ºC. The pressure decay curve was monitored until a steady-state pressure was reached, with typical equilibration times of 10-15 hours. The gas solubility was calculated based on the change in pressure in the cell headspace and the ideal gas law based on the known headspace volume.
**Figure S3.** Calculation of diffusion coefficient ($D$, m$^2$ s$^{-1}$) of SF$_6$ at 298 K. Stokes equation:

$$D = \frac{k_B T}{6\pi \eta a}$$

where $\eta$ = dynamic viscosity of TEGDME (4.05 × 10$^{-3}$ Pa·s)$^2$ and $a$ = hydrodynamic radius ($a$ = 121 pm for O$_2$ and $a$ = 160 pm for SF$_6$).

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<td>O$_2$</td>
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<tr>
<td>SF$_6$</td>
<td>3.37 × 10$^{-6}$</td>
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**Figure S4.** a) Photograph of freshly rolled Li before (left) and after (right) exposure to SF$_6$ gas for approximately 24 hours. b) OCV measurements of pre-passivated Li electrodes in electrolyte (0.3 M LiClO$_4$ in TEGDME) before and after purging with SF$_6$. The minor fluctuations in potential (< 5 mV) over a 24-hour span following purging of the gas are related to ambient temperature variations. c) Photograph of stabilized Li exposed to SF$_6$ (left) and after (right) full discharge in Swagelok cell with SF$_6$ headspace.
Figure S5. a) Schematic representation of a Li-SF₆ cell. b) Schematic of a Li-SF₆ cell consisting of a pre-passivated Li electrode and Vulcan carbon-based cathode with SF₆ dissolved in the electrolyte. During discharge, \( n \) electrons (1 < \( n \) < 8) and Li⁺ ions react with SF₆ and form equivalents of LiF and lower fluorides of SF₆ (SF₇\(_m\), 1 < \( m \) < 5), S or Li₂S.

Figure S6. Argon-only discharge in TEGDME electrolyte at a) 7.5 mA g\(^{-1}\) and b) 75 mA g\(^{-1}\).
**Figure S7.** Impedance spectra of as-assembled Li-SF₆ cells for the two electrode architectures used in this work (EIS: 10 mV perturbation from 1 MHz to 100 mHz at open circuit voltage).

**Figure S8.** In situ pressure monitoring during discharge at 75 mA g⁻¹ on Celgard-supported cathodes.
Figure S9. $^1$H NMR of fully discharged electrodes (75 mA g$^{-1}$) following rinsing in D$_2$O. ii) Discharge in TEGDME to ~1300 mAh g$^{-1}$. For comparison, reference spectra of i) 15 µL of 0.3 M LiClO$_4$ in TEGDME (dissolved in 1 mL D$_2$O) are shown. TFE was added into the D$_2$O-washed electrolyte samples to provide a quantitative concentration scale for possible contaminants.

Figure S10. a) $^{19}$F NMR validation curve obtained by dissolving known amounts of LiF and TFE in D$_2$O (the typical solubility of LiF in H$_2$O is ~50 mM$^3$ and TFE is completely miscible in H$_2$O). Note, the curve was not used for determining the amount of LiF from the discharged cathodes but rather, to illustrate the quantification technique is valid for the ranges of LiF concentrations measured. The red line indicates a slope of 1. b) $^{19}$F NMR spectra of D$_2$O-washed cathodes discharged at 75 mA g$^{-1}$ in TEGDME to ~1490 mAh g$^{-1}$ (expected relative integrated ratio = 17.64). The measured LiF quantity corresponded to 28.72 µmol LiF mAh$^{-1}$. 
Figure S11. High resolution S 2p XPS spectra of commercially available a) Li$_2$S and b) S$_8$ (supplier: Sigma Aldrich).
Figure S12. High resolution C 1s XPS spectra corresponding to the data in Figure 6 in the main text. (a) Pristine Vulcan carbon electrode; (b-d) Electrodes discharged at 75 mA g\textsuperscript{−1} in 0.3 M LiClO\textsubscript{4} in TEGDME (capacity = 1290 mAh g\textsuperscript{−1}) at different sputtering times.
Figure S13. Comparison of rotating disk cyclic voltammetry of SF$_6$ – saturated electrolytes on GC electrodes (20 mV s$^{-1}$ scan rate) in TEGDME at a) 0 and b) 900 rpm.

Figure S14. Galvanostatic discharge and charge attempt of a Li-SF$_6$ cell at 75 mA g$_{C}^{-1}$. 
**Figure S15.** (a) CV scan conducted at a slower scan rate of 5 mV s\(^{-1}\). (b) CVs in SF\(_6\)-saturated electrolytes of the first and second scan in TEGDME at 20 mV s\(^{-1}\).

**Figure S16.** Argon-only discharge in DMSO electrolyte (0.3 M LiClO\(_4\)) at 30 mA g\(_c\)\(^{-1}\).
References:

