The Application of Redox Targeting Principles to the Design of Rechargeable Li–S Flow Batteries

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Battery electrical energy storage (BEES) has become an integral component of many of today’s energy systems where renewable but intermittent energy sources are increasingly used for power generation. While “numbering up” (aggregation of smaller systems) is the universal approach to increase the BEES size at the system level, upscaling at the cell level varies with the battery technology and is most easily done in the redox flow batteries (RFB). This is because unlike a conventional battery cell where energy and power characteristics are mutually compensating, the RFB can achieve complete decoupling of power and energy in a single cell: the capacity of a RFB is limited only by the size of the reservoirs where dissolved species capable of highly reversible redox reactions are stored, whereas the power of a RFB depends on the electrode area which can be scaled independently of the reservoirs. This flexibility also introduces its own constraint: in addition to the electrode potential of the redox species, the energy density of a RFB is also limited by the solubility of the redox species in the electrolyte. For example the vanadium redox flow battery, one of the most common RFB, has an energy density of only 29 Wh kg⁻¹.[1,2] The current research in RFB is therefore focused on new battery chemistry and/or new system configuration to address this major inadequacy.

Rechargeable lithium batteries are well known for their high energy density. Among them the lithium–sulfur (Li–S) batteries have drawn strong recent interest as the successor to the highly successful lithium-ion batteries (LIB). Li–S batteries use sulfur, a low cost, high capacity, and safe cathode material to achieve a very high theoretical energy density of ≈2600 Wh kg⁻¹.[1,2] However, poor ionic and electronic conductivities of sulfur, as well as sulfur dissolution (as polysulfides) during battery operation, are the disadvantages of Li–S batteries. As counter measures sulfur encapsulation in a conducting matrix together with sophisticated containment techniques have been proposed;[3] albeit at the expense of a reduced energy density. Li–S batteries have to be substantially improved before they can be used for the large scale storage of electrical energy.

There have been some efforts to run the Li–S or LIB as a RFB.[5–16] For example, Yang et al.[5] reported a lithium/poly-sulfide RFB which was designed to cycle between Li₂S₈ and Li₂S₄ (where all redox species are soluble). This operation however limits the capacity to be as low as 210 mAh g⁻¹, or one eighth of the theoretically capacity of the S cathode if the latter is allowed to discharge to Li₂S (1675 mAh g⁻¹). The Chiang group at Massachusetts Institute of Technology (MIT) used a polysulfide slurry as the catholyte and a large quantity of nanoscale carbon as extended electrode, to enable the cycling of polysulfides deep into the precipitation regime (and yet electronically connected) to improve the capacity utilization to 1200 mAh g⁻¹ (vs 1460 mAh g⁻¹ theoretically from Li₂S₈ to Li₂S).[6] The most interesting recent development is the concept of “redox targeting reactions” proposed by Wang et al., where fast diffusing relay molecules (“redox mediators”) are used to extract/inject charges with insulating or poorly conducting Li⁺ storage hosts.[7] The group successfully demonstrated the concept by identifying the redox mediators for selective cathode and anode Li⁺ storage compounds, such as LiFePO₄[8] and TiO₂[9] Inspired by these discoveries, we envisage the possibility of applying the same redox targeting concept to address the operational issues in Li–S batteries. The resulting hybrid battery system is termed as “redox targeting Li–S flow battery” in order to differentiate it from the “redox flow Li–S batteries” in the current literature.

The central concept in redox targeting is the use of a pair of redox mediators to straddle the redox reactions involving a lithium storage host. Herein, we demonstrate the use of bis-(pentamethyl-cyclopentadienyl) chromium (CrCp*₂) and bis-(pentamethyl-cyclopentadienyl) nickel (NiCp*₂) as tandem mediators for the S + 2e⁻ + 2Li⁺ ↔ Li₂S reaction. Sulfur is stored in an energy tank and by design is not a flow component. The redox mediators are used to extract/inject electrons with the Li⁺ storage compound in the energy tank. Hence, unlike a typical RFB the performance of this redox targeting system is not constrained by the solubility of the redox active species (mediators) in the electrolyte since the mediators are charge transfer agents and charge transporters and not the energy storage compounds. As shown in Figure 1, at the start of the discharge reaction, mediator CrCp*₂ reacts chemically with the S cathode in the energy tank, driven by the difference in their electrode potentials. In the process CrCp*₂ is oxidized to CrCp*₂⁺ while S is reduced to polysulfides or sulfide. The oxidized species CrCp*₂⁺ flows to the central electrochemical cell where it is reduced at the cathode to CrCp*₂⁻ (by the electrons from the Li metal anode) and returns to the energy tank to start the next round of reaction. The other mediator NiCp*₂⁻ is locked in the reduced state because of the electrode potential relation E[Cr(III)Cp*₂⁻/Cr(II)Cp*₂] < E(S/Li₂S) < E(Ni(III)Cp*₂⁻/Ni(II)Cp*₂⁻) and does not participate in electron extraction/injection. During charging, NiCp*₂⁻ is oxidized to NiCp*₂⁺ in the central electrochemical cell, and flows to the energy tank where it oxidizes the discharge products of the sulfur cathode.
(mostly sulfide). NiCp₂ is regenerated in this chemical reaction and flows back to the central electrochemical cell where it is reoxidized to NiCp*₂⁺ for a second round of chemical reaction. CrCp₂ stays as CrCp*₂⁺ in these processes but is otherwise nonparticipative due to the above electrode potential relation. Battery cycling therefore involves charge and discharge processes mediated through two coupled electrochemical–chemical reactions of the redox mediators.

The paired redox mediators are central to the effective lithiation of sulfur and delithiation of lithium sulfide via the redox targeting reactions in the energy tank. Cyclic voltammetry (CV) was used to screen for the paired redox couples and to evaluate the reversibility of their redox reactions. After a large number of trials, two redox mediators, CrCp*₂ and NiCp*₂, with the reduction peak potential of 1.96 V and NiCp*₂ with the oxidation peak potential of 2.49 V (vs Li/Li⁺) respectively, were found to straddle the potential window over which the S/Li₂S transformation occurs (Figure 2a). In the measurements an S-based copolymer (poly (sulfur-random-1,3-diisopropenylbenzene) or poly(S-r-DIB) in brief) was used in lieu of elemental sulfur to minimize the sulfur dissolution problem (dissolved polysulfides could migrate to the Li anode and from an electrochemically inactive layer to degrade the battery performances). In addition to the matching redox potentials, high reversibility and fast ionic diffusion are also desired for the redox mediator molecules. Figure 2b shows that at the scan rate of 50 mV s⁻¹, the voltammograms of the 5th, 100th, 200th, 300th, and 400th cycles are almost completely superimposable, an indication of high electrochemical stability and independent operability of these redox couples. The peak separations of the redox mediators in the scan rate range of 5 to 100 mV s⁻¹ (Figure S1a,b, Supporting Information) are typical of reversible one-electron charge transfer reactions. The anodic and cathodic peak currents (iₚ) are proportional to the square root of the scan rate (Figure S1c,d, Supporting Information) (v) where diffusion coefficients of ≈5.8 × 10⁻⁶ for CrCp*₂ and 6.7 × 10⁻⁶ cm² s⁻¹.

Figure 1. a) Schematic of a redox targeting lithium–sulfur flow battery. b) Illustration of the redox reactions occurring in the sulfur tank during discharge and charge. In this configuration, two redox mediators, bis-(pentamethyl-cyclopentadienyl) chromium (CrCp*₂) and bis-(pentamethyl-cyclopentadienyl) nickel (NiCp*₂) are used in tandem as dissolved species in the electrolyte. The redox targeting reactions between the redox mediators and sulfur occur in the energy tank, whereas the regeneration of the redox mediators occurs in the central electrochemical cell.

Figure 2. a) Cyclic voltammogram of 10 × 10⁻³ m CrCp*₂ and 10 × 10⁻³ m NiCp*₂ in 1.0 m LiTFSI/TEGDME electrolyte on a glassy carbon working electrode at 50 mV s⁻¹ (the olive curve). For comparison the cyclic voltammogram of poly(S-r-DIB), an S-based copolymer is also shown (the orange curve). b) Cyclic voltammograms of the two redox mediators in the 5th, 100th, 200th, 300th, and 400th cycles at 50 mV s⁻¹.
for NiCp²⁺ could be calculated from the Randles–Sevcik equation. These values are comparable to that of ferrocene (4.6 × 10⁻⁶ cm² s⁻¹), the most common redox shuttle molecule used for redox targeting.[19,20]

The voltammetry results suggest that targeting reactions between the sulfur cathode and the redox mediator molecules are thermodynamically feasible. For confirmation of actual battery action, a redox targeting flow battery was constructed using poly(S-r-DIB) as the energy storage compound in the energy tank, and graphite felt cathode and hybrid lithium-metal anode[21] for the central electrochemical compartment. The electrolyte was 10 mL of 10 × 10⁻³ M CrCp²⁺, 10 × 10⁻³ M NiCp²⁺, 1.0 M LiTFSI, and 5 wt% LiNO₃ (additive) in a TEGDME solvent. A 5 wt% LiNO₃ was also used as additive to inhibit the reactions between the Li metal surface and adventitious polysulfide species.[22]

Figure 3a shows that in the absence of an active cathode material (the S-based copolymer), two pairs of voltage plateaus appeared during charge and discharge, corresponding to the reduction and oxidation of the two redox mediators, respectively. In the first charge process, the oxidation of CrCp²⁺ to CrCp²⁺⁺ gave rise to the first voltage plateau at ≈1.95 V (step I), followed by the oxidation of NiCp²⁺ to NiCp²⁺⁺ at ≈2.42 V (step II). The two voltage plateaus in the discharge at ≈2.30 and 1.85 V were due to the reduction of NiCp²⁺⁺ to NiCp²⁺ (step II') and CrCp²⁺⁺ to CrCp²⁺ (step I'), respectively. The clean separation of these voltage plateaus indicates that the two mediators acted independently of each other. The electrochemical reactions involved may be categorically written as

**Charge:**

\[ \text{Cr}(\text{Cp})^+ \rightarrow \text{Cr}(\text{Cp})^0 ; \text{Ni}(\text{Cp})^+ \rightarrow \text{Ni}(\text{Cp})^0 \]

**Step I**

**Step II**

**Discharge:**

\[ \text{Ni}(\text{Cp})^0 + \text{e}^- \rightarrow \text{Ni}(\text{Cp})^+ ; \text{Cr}(\text{Cp})^0 + \text{e}^- \rightarrow \text{Cr}(\text{Cp})^+ \]

When 12.2 mg of poly(S-r-DIB) (corresponding to 10.0 mg sulfur) was added at the end of discharge of the redox species, discharge was extended nearly eight folds due to the chemical reaction between CrCp²⁺ and poly(S-r-DIB) (Figure 3b). In this process, CrCp²⁺ was oxidized to CrCp²⁺⁺ by poly(S-r-DIB) in the energy tank, and the oxidized CrCp²⁺⁺ was reduced back to CrCp²⁺ in the central electrochemical reactor by the electrons released from Li metal dissolution in the hybrid anode compartment. The discharge process led to the reduction and lithiation of poly(S-r-DIB) in the energy tank and the formation of DIB-bound sulfur products as well as low-order insoluble sulfides (i.e., Li₂S₃, Li₂S₂).[23] Polysulfide dissolution was suppressed by such an approach but not completely eliminated.

In the subsequent charge process, CrCp²⁺ was oxidized first to CrCp²⁺⁺. This is shown by the first short charge plateau at ≈2.0 V in Figure 3b. NiCp²⁺ was then oxidized in the central
compartment, reduced by the discharged sulfur products in the energy tank, and then regenerated in the central compartment to complete the cycle. This is shown by the long and main charge plateau at ≈2.5 V. The last charge plateau at ≈2.8 V could be due to the oxidation of migrant higher polysulfides directly to S in the central compartment. As a result, the poly(S-r-DIB) cathode could be progressively lithiated to discharged organosulfur DIB products and insoluble low-order polysulfides during discharge, and delithiated reversibly in the following charge cycle. The first discharge capacity was about 766 mAh g⁻¹, corresponding to 0.92 e⁻ per S atom, suggesting that insoluble Li₂S₂ was the main discharge product. The low sulfur utilization was likely caused by the relatively large size of poly(S-r-DIB) (tens of micrometers, Figure S2, Supporting Information) where the copolymer interior contributed little to the reaction with the redox mediator molecule. 

It is to be expected that cell performance would depend on the mediator concentration, flow rate, and their combinations. After some preliminary optimization attempts, the combination of 10⁻³ M and 15 mL min⁻¹ was found to provide a reasonably good performance. Figure 4a shows the cycling performance of the redox targeting flow battery formulated with these operating parameters at the current density of 0.32 mA cm⁻². The rate of capacity decay was 2.43% per cycle for the first 20 cycles; and 0.76% per cycle from the 20th to the 100th cycle. The large capacity decay should originate from polysulfide dissolution, since the driving force in the redox targeting reaction from S to Li₂S by CrCp₂⁺ (100 mV) may be too low to effectively inhibit lithium polysulfide formation. Coulombic efficiency was above 99.5% after the first 5 cycles, and energy efficiency (EE) as high as 75% could be obtained. When the discharge/charge current density was increased to 1.02 mA cm⁻², the electrochemical behavior was mostly the same except for a lowering of EE to 64%. While these results may not impress in the absolute sense; they do surpass the performance of recently reported nonaqueous vanadium or lithium-ion flow batteries based on organic redox species where the typical EE is below 50%.²⁴⁻²⁶ The prevailing view suggests that the inefficiency could be caused by the resistivity of the membrane separating the hybrid anode and cathode compartments. When poly(S-r-DIB) was replaced by a commercial S powder, a more drastic and protracted capacity decay (5.75% per cycle and 10 cycles for stabilization) was observed (Figure S3, Supporting Information), mostly due to the unrestrained dissolution of polysulfides. The tandem use of these mediators is expected to reduce the problems of polysulfide dissolution since the mediators could also reduce/oxidize soluble polysulfides to Li₂S/S during discharge and charge. On the other hand the permeation of mediators and polysulfides through the membrane to the anode compartment cannot be prevented in the current implementation, which resulted in the observed capacity decay. These results indicate that there is more to be desired for the sulfur encapsulation technique. In order to identify the major cause for capacity decay (polysulfide dissolution or mediator deactivation), fresh cathode material was added to the energy tank after prolonged cycling when capacity fading had occurred. For example, Figure 4b shows that the addition of another batch of

![Figure 4](https://www.MaterialsViews.com)
of redox couples, CrCp*$_2$ and NiCp*$_2$ which could straddle the cathode material. This was accomplished by identifying a pair with flat voltage profiles and high stability of the redox mediators. Admittedly the specific energy of this redox targeting battery at the present stage of development is less than satisfactory. This study however demonstrated the salient advantages of this design over conventional Li–S batteries—the elimination of conductive additive in the sulphur electrode (~30 wt%); and easy scalability. Different from a conventional RFB, energy density is not dependent on the solubility of the redox active species in the electrolyte and volumetric energy density can be very high depending on the cell design. More importantly, the redox targeting approach has a notable advantage over conventional flow battery designs using dissolved polysulphides or semi-solid flows—the avoidance of pumping a viscous fluid or slurry of suspended solids with issues such as high energy cost and channel blockage. On the other hand, polysulphide dissolution during battery discharge and charge remains an issue since it increases electrolyte viscosity (and hence the pumping energy requirement) and could also cause flow channel blockage in prolonged operations. While the use of mediator molecules reduces the adverse effects to a great extent (i.e. soluble polysulphides can continue to react with the mediators dissolved in the electrolyte), effective sulfur-encapsulation techniques or the use of polysulphide-insoluble electrolyte are still the long-term solutions. There are some encouraging recent developments such as the use of sulphophilic host materials Ti$_4$O$_7$ and δ-MnO$_2$ for strong polysulphide/Li$_2$S binding and subsequently high capacity retention.$^{[27,28]}$ Another important aspect is the development of high selectively Li$^+$-conducting membrane separator to reduce self-discharge due to mediator crossover to the Li anode. The latter is an ongoing research activity in our laboratory and we have some interesting results to report in a different article.

Conclusions

In summary, we have successfully applied the redox targeting concept to rechargeable Li–S batteries, enabling the latter to operate with a poorly conducting or a totally insulating S/Li$_2$S cathode material. This was accomplished by identifying a pair of redox couples, CrCp*$_2$ and NiCp*$_2$, which could straddle the S/Li$_2$S redox reactions in battery charging/discharging. Preliminary battery tests showed some promising results such as flat voltage profiles and high stability of the redox mediators. The cell components at this stage of development have yet to be fully optimized and hence parasitic effects such as polysulphide dissolution and mediator and polysulphide crossover through the membrane to the Li anode are still evident after a sufficiently long operation. The redox targeting Li–S battery does inherit the intrinsic benefits of flow batteries in terms of the decoupling of power and energy; and simpler scalability at the cell level. It is our hope that more can be done to explore the principle of redox targeting as an alternative approach to developing rechargeable Li–S batteries.

Experimental Section

Chemicals, Materials Synthesis and Characterization: Lithium foil (99.9% metal basis, thickness 0.75 mm), LiTFSI (~99%), TEGDME (~99%), lithium nitrate (99.99%), and sublimed sulfur (~99.5%), were purchased from Sigma-Aldrich. DIB (97%) and the two finally selected redox molecules, CrCp*$_2$ (97%) and NiCp*$_2$ (97%) were supplied by Strem Chemicals Inc. All chemicals were used as received.

A sulfur-based copolymer poly(S-r-DIB) was synthesized by the procedures reported by the Pyun group.$^{[17]}$ In a typical preparation, sublimed sulfur (4.5 g) was introduced in a 26 mL glass vial and heated to 165 °C with stirring in an oil bath until a molten orange liquid was formed. DIB (97%, 1 mL) was then pipetted into the vial. Heating was continued to 170 °C and then kept at this temperature for 10 min; the product was quickly removed from the vial using a spatula and then cooled to room temperature naturally.

Field emission scanning electron microscopy was carried out on a JEOL JSM-6700F microscope operating at 5 kV. X-ray photoelectron spectroscopy was performed on a Kratos Axis Ultra Delay-Line Detector (DLD) spectrometer.

Electrochemical Measurements: The electrolyte preparation, the assemblies of the CV cell and flow cell were all carried out in an argon-filled MBRAUN glove box where the moisture and oxygen levels were below 1 ppm. The cyclic voltammograms of the redox molecules were measured in a modified three-electrode system, using a glassy carbon disc working electrode, a Pt foil counter electrode and a Li metal reference electrode. The electrolyte consisted of 10 × 10$^{-3}$ M CrCp*$_2$, or/and 10 × 10$^{-3}$ M NiCp*$_2$, 5 wt% LiNO$_3$ and 1.0 M LiTFSI in TEGDME (a more dilute electrolyte (5 × 10$^{-3}$ M CrCp*$_2$ or/and 5 × 10$^{-3}$ M NiCp*$_2$, 2.5 wt% LiNO$_3$ and 0.25 M LiTFSI) was used for the determination of diffusion coefficients by the Randles–Sevcik equation. CV was performed on an Auto Lab FRA2 type III electrochemical system.

The flow cell was made up of two major components—an energy storage tank with a filter to prevent S or S copolymer from leaving the tank, and a central electrochemical cell formed by a graphite felt cathode and a “hybrid anode” (stacked graphite felt, Celgard 3501 separator, and Li metal disc)$^{[21]}$ (Figure S5, Supporting Information). The active contact area in the central cell was ~920 mm$^2$, or 3.14 cm$^2$. Electrolyte was circulated between the energy tank and the central electrochemical cell at 15 mL min$^{-1}$ (120 rpm) by a peristaltic pump. The charge/discharge behavior of the flow cell was measured by a battery tester (NEWARE BTS-SV, Neware Technology Co., Ltd.) in the voltage window of 1.5–3.0 V, by injecting catholyte (10 mL) containing 10 × 10$^{-3}$ M CrCp*$_2$, or/and 10 × 10$^{-3}$ M NiCp*$_2$, 5 wt% LiNO$_3$, and 1.0 M LiTFSI in TEGDME.
Supporting Information


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Figure S1. Cyclic voltammetry of 5 mM CrCp*₂ (a) and 5 mM NiCp*₂ (b) in 0.25 M LiTFSI/TEGDME at different scan rate: 5, 10, 20, 30, 40, 50, 100 mV s⁻¹; (c) and (d) Peak current I_p as a function of the square root of scan rate ν₁/₂.

Figure S2. (a) Typically FESEM image of the poly(S-r-DIB) copolymer; (b) S 2p X-ray photoelectron spectra of poly(S-r-DIB) copolymers which agree well with the Pyun report.¹
Figure S3. Cycle stability of a redox targetting flow cell using commercial S powder as the active material at 0.32 mA cm\(^{-2}\).

Figure S4. (a) SEM images of Li anode before and after 100 cycles. (c) Experimental demonstration of the power of the cell to light up eight LED bulbs simultaneously.
**Figure S5.** Schematic diagram of the central electrochemical compartment. The raised circular area in the end plate is ~20 mm in diameter with an active contact area of 3.14 cm$^2$. The dimension of the carbon felts is $\Phi19 \times 3.0$ mm. The two carbon felts are tightly stacked in the compartment.

**Reference**