

THE ELECTROCHEMICAL BEHAVIOR OF POLYSULFIDES IN TETRAHYDROFURAN

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Summary

The oxidation-reduction process of sulfur and polysulfides was studied at a glassy carbon electrode in 1M LiClO₄-THF solution using a programmed cyclic voltammetry technique. Over the range 1300 to -2000 mV (*vs.* porous carbon in lithium polysulfide solution), one anodic and up to three cathodic peaks were found. All of them correspond to irreversible processes. Kinetic parameters were evaluated and plausible mechanisms have been suggested.

Introduction

The Li/S organic battery consists of a lithium anode and a porous, Teflon-bonded, carbon cathode which is loaded with sulfur or polysulfides. The electrolyte is a lithium polysulfide saturated solution of 1M LiClO₄ in a THF-toluene mixture. The cell exhibits, at low drain, a very high energy density [1, 2]: 730 W h/kg or 950 W h/l at room temperature, and 950 W h/kg or 1200 W h/l at 60 °C (calculated on the basis of all cell components, excluding the case). Its self discharge rate is very low and depends on electrolyte composition. The lowest measured self discharge was 1.3% per month at 60 °C (during discharge at 12 μA cm⁻²). This is equivalent to a shelf life (or low rate operation time) of 25 years at room temperature, and was accomplished by the use of an electrolyte in which the solubilities of both Li₂S and lithium polysulfides are limited. In contact with such an electrolyte, the lithium anode becomes covered by an Li₂S passivating layer which acts as a solid electrolyte interphase (SEI). Thus the Li/S battery belongs to the SEI battery family [3].

The feasibility of the Li/lithium polysulfide-THF/C system to function as a secondary battery was studied recently [4, 5]. At a low drain and elevated temperature, the cycling efficiency of the polysulfide electrode was close to 100% [4]. We have recently found that the Faradaic efficiency for the reduction of polysulfides in the Li/S organic cell is above 95% at cell voltages higher than 2 V [1, 2]. The polysulfide reduction mechanism is expected to be very complicated because:

- (i) it is a multielectron process;
- (ii) in organic solvents, there are many equilibrium reactions between polysulfides and soluble sulfur [6];
- (iii) low dielectric solvents, such as ethers and toluene, favor the formation of ionic aggregates [7].

The goal of this work was to study the redox behavior of polysulfides in THF using a programmed cyclic voltammetry technique.

Experimental

All solutions were prepared and cells were assembled within an argon-filled glove box. Details regarding these procedures appear in refs. 1 and 2. Programmed cyclic voltammetry experiments were carried out inside the glove box, at a glassy-carbon electrode, in THF solutions of 0.8M LiClO₄ and lithium polysulfide at varying concentration and sweep rate. The micro-computer-based cyclic voltammetry technique was described in refs. 8 and 9.

The electrochemical cell consisted of a glassy carbon working electrode, a stainless steel counter electrode, and a reference electrode in a separate compartment. The reference electrode consisted of a porous, Teflon-bonded carbon electrode immersed in a THF solution of 0.8M LiClO₄ and 4mM Li₂S₆. It was found that this reference electrode shows Nernstian behaviour and that its potential is reproducible and stable to better than 0.1 mV. Prior to each set of experiments the glassy carbon electrode was polished with fine alumina powder (0.05 μm particle size), washed with distilled water and AR acetone, and introduced into the glove box.

Results and discussion

The cyclic voltammogram of 4mM Li₂S₁₂ can be seen in Fig. 1. This is a typical voltammogram for polysulfides having a chain length of 7 - 12. It contains one anodic peak, an anodic shoulder near 0 V and three cathodic peaks. A voltammogram of Li₂S₆ does not contain the first cathodic peak. It is interesting to note that while the complete reduction of polysulfides is carried out in three steps, their oxidation to elemental sulfur needs one step only.

The separation between the anodic peak and the first cathodic peak is very large, more than 350 mV at a sweep rate of 2 mV s⁻¹, and it increases with the sweep rate. This indicates an irreversible process.

The plot of anodic peak current density ($I_{p,a}$) vs. concentration of polysulfide yields a straight line with a slope of 1.0 ± 0.1 (Fig. 2) as expected for a diffusion controlled process. The plot of $I_{p,a}$ vs. log (sweep rate) (Fig. 3) yields a straight line with a slope of 0.45 ± 0.03 . This value is significantly smaller than 0.5, indicating a complex process in which a chemical reaction may precede an irreversible charge transfer step.

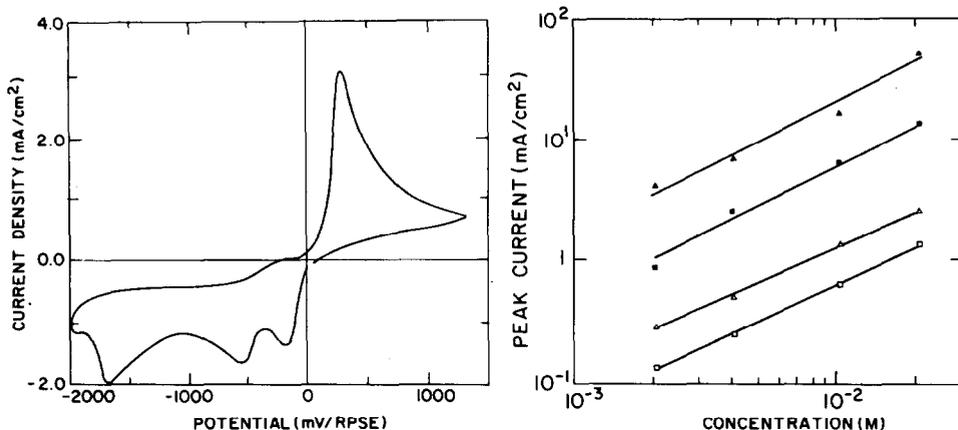


Fig. 1. Cyclic voltammogram of 4mM Li_2S_{12} in 0.8M LiClO_4 -THF solution. Sweep rate: 50 mV/s; cathodic direction.

Fig. 2. Anodic peak current density as a function of the concentration of $\text{Li}_2\text{S}_{8,4}$. Sweep rates (mV/s): \square - 2, slope 1.01; \triangle - 12, slope 0.93; \blacksquare - 200, slope 1.08; \triangle - 3800, slope 1.08.

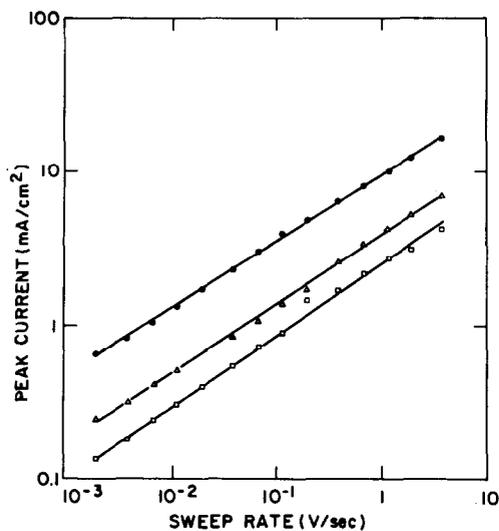


Fig. 3. Anodic peak current density as a function of sweep rate (log scales). Concentration of polysulfide $\text{Li}_2\text{S}_{8,4}$: \square , 2mM; \triangle , 4mM; \bullet , 10mM.

The Tafel slope for the oxidation process of polysulfides was found to be 120 - 130 mV. It was calculated in three ways:

(i) from the plot of $\log(I_a)$ vs. η ;

(ii) from the plot of $\log(E_{p,a})$ as a function of $\log(\text{sweep rate})$ - this yields a straight line whose slope is one half the Tafel slope (Fig. 4);

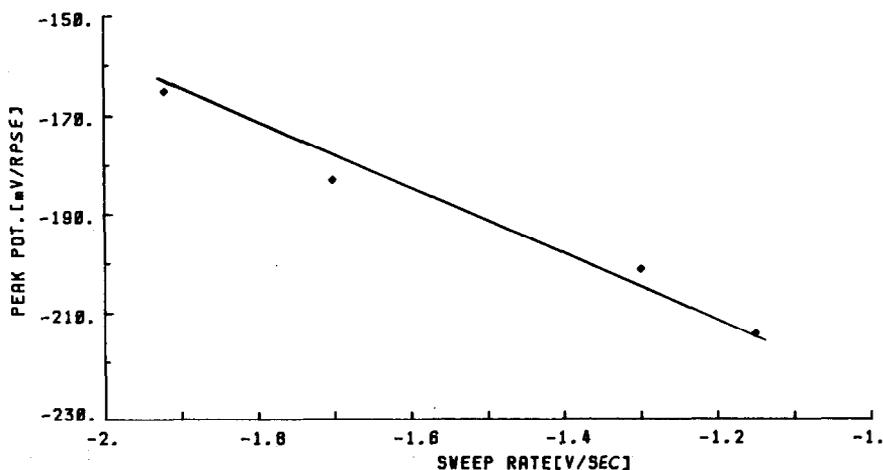
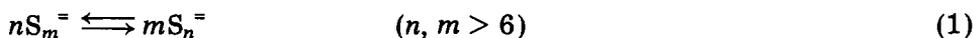


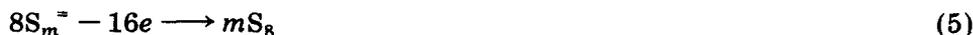
Fig. 4. First cathodic peak potential as a function of log (sweep rate) for Li_2S_{12} (THF solution, polysulfide concentration: 4mM. Slope = 60).

(iii) from the difference $E_p - E_{p/2}$. A diffusion coefficient for polysulfides of $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was calculated from the current peak and this Tafel slope using an equation for irreversible processes.

The following plausible oxidation mechanism may account for this Tafel slope and the other kinetic parameters:



The overall reaction is:



As we have only one major anodic peak for all polysulfides, it seems that one of the polysulfides has the fastest kinetics and the anodic peak is due to its oxidation (reactions (2) and (3)). Other polysulfides are transformed to it by reaction (1) which precedes the charge transfer step. It is suggested that the rate determining step for the oxidation process is the first charge transfer step (reaction (2)), while the second step seems to be faster as the reactant is an unstable radical-ion while the product is a stable sulfur molecule.

The reduction process is much more complicated and far from being well understood. The voltammogram of elemental sulfur in the cathodic direction (Fig. 5) is very similar to that of polysulfides (Fig. 1). Each of the four current peaks appears at the same potential as the corresponding peak

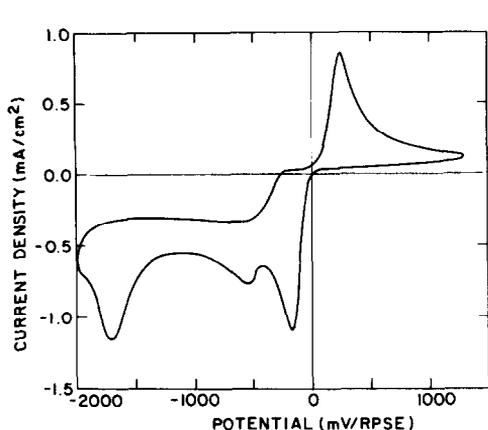


Fig. 5. Cyclic voltammogram of 4mM S_8 in 0.8M $LiClO_4$ -THF solution. Sweep rate: 20 mV/s; cathodic direction.

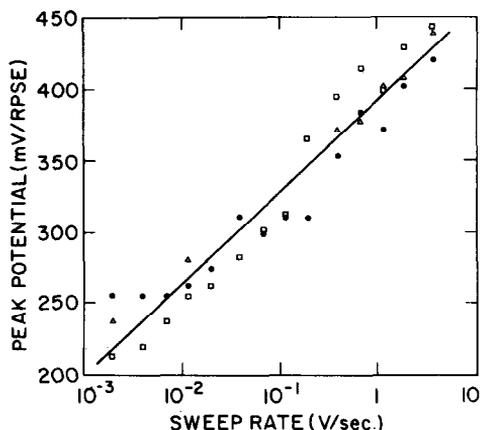


Fig. 6. Anodic peak potential as a function of \log (sweep rate) for $Li_2S_{8.4}$ (THF solutions). Polysulfide concentration: \square , 2mM; \triangle , 4mM; \bullet , 10mM. $b = 2 \times \text{slope} = 125$ mV/decade.

in the voltammogram of polysulfides (at the same sweep rate and concentration). The Tafel slope for the first reduction peak of both sulfur and polysulfides is 120 - 130 mV. This can be calculated from Fig. 6. The cathodic peak current density (first peak) ($I_{p,c,1}$) was found to increase linearly with the logarithm of polysulfide concentration (Fig. 7). However, the slope of this line was smaller than unity (0.8 ± 0.1), implying a complex reaction mechanism. On the other hand, the plot of $\log(I_{p,c,1})$ vs. \log (sweep rate) yields a straight line with a slope of 0.5 ± 0.03 , indicating a diffusion controlled process (Fig. 8).

The diffusion coefficient of polysulfides was also calculated from the first cathodic peak and the experimental Tafel slope using an equation for irreversible processes. The value obtained was $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, similar to that calculated from the anodic peak.

The following plausible reduction mechanism may account for the first reduction step of sulfur and polysulfides:



The overall reaction for sulfur is:



The overall reaction for polysulfide is



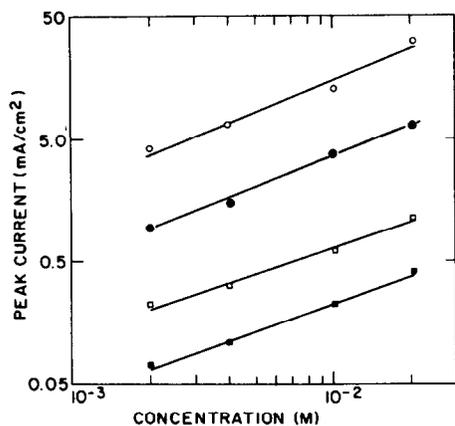


Fig. 7. Cathodic peak current density (first peak) as a function of concentration of $\text{Li}_2\text{S}_{3.4}$. Sweep rates (mV/s): ■ — 2, slope = 0.77; □ — 12, slope = 0.72; ● — 120, slope = 0.83; ○ — 3800, slope = 0.87.

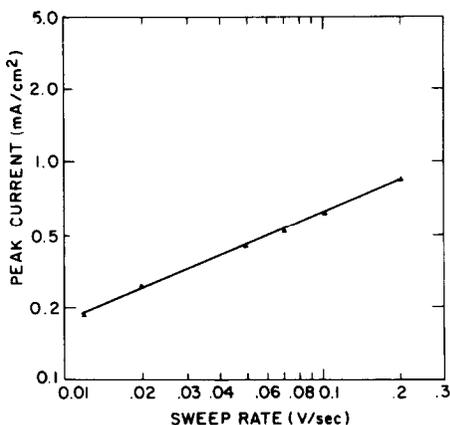


Fig. 8. Cathodic peak current density (first peak) as a function of sweep rate for 4mM Li_2S_8 . Slope = 0.52.

Although this mechanism was written for $\text{S}_8^{=}$, it may be the same for all polysulfides having a chain-length higher than 6.

This mechanism is in agreement with the conclusion of Rauh *et al.* [6] that polysulfides of chain length less than 5 - 6 must have low stability and are poorly soluble in THF.

The reactions which correspond to the second and third cathodic peaks are not fully understood. The overall reaction corresponding to the second peak seems to be the reduction of $\text{S}_6^{=}$ to $\text{S}_4^{=}$. Li_2S_4 has a low solubility in the solution and thus may, at least partially, precipitate on the electrode surface. The overall reaction corresponding to the third peak may be a further reduction of $\text{S}_4^{=}$ to $\text{S}^{=}$ which precipitates as an Li_2S film on the electrode surface.

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