

Dissolution and Reprecipitation of Sulfur on Carbon Surface

Jingdong Liu (✉ ljd@fzu.edu.cn)

Fuzhou University - Yishan Campus: Fuzhou University

Yuanhui Zheng

Fuzhou University - Yishan Campus: Fuzhou University

Short Report

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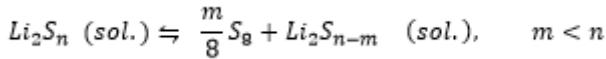
Abstract

Further understanding of the redox process of lithium polysulfides (PSs) on carbon surface is helpful to design Li/S batteries with better performance. "Shuttle mechanism" can explain the low coulomb efficiency and self-discharge of a Li/S battery, but it cannot explain the fact that battery performance is closely affected by electrolyte volume and sulfur load. This paper aims to reveal main redox process of PSs on surface of carbon by examining cathodic behavior with different electrolyte volume and sulfur load. SEM photos and Impedance Spectra of cathode before and after 1st discharge were compared, it was found that the discharge process is the continuous dissolution of sulfur composites with carbon into the electrolyte to form PSs, at the same time, PSs re-precipitates sulfur on the surface of cathode through disproportionation reaction to form a solid film. CV curves showed that the solid film passivates electrode, and the electrode is activated only when potential sweeps negatively and Li_2S is generated. When lean electrolyte is used, there is fluctuation in CV curves, which proves that the dissolution-reprecipitation of sulfur is the main process of cathode. The discharge-charge curves of cathodes with different sulfur load were compared, it was found that there is wavy fluctuation in the discharge curve with high sulfur load, which proves again that the sulfur reaction dominates the electrode process.

1. Introduction

A better understanding on reaction mechanism of a Li/S battery is helpful to design a battery with better performance. [1–2] In the past, people used the mechanism similar to that of a lithium-ion battery to describe the process of a Li/S battery, that is, lithium ions shuttle back and forth between the positive and negative electrodes to realize energy conversion. Later, it was recognized that the intermediate product of discharge—lithium polysulfides(PSs), is dissolved in the electrolyte and shuttle back and forth between the positive and negative electrodes, that is, the so-called "shuttle mechanism", so as to explain the low coulomb efficiency and capacity attenuation of a Li/S battery. [3–5] "shuttle mechanism" can explain the self-discharge and low coulombic efficiency of a Li/S battery, but the redox process of PSs described by "shuttle mechanism" is inconsistent with its CV curves. It was believed that PSs is reduced to Li_2S_4 first and then further reduced to Li_2S and Li_2S_2 based on "shuttle mechanism". Nevertheless, CV curves of PSs show two reduction peaks and one oxidation peak in usual reports. [6–7] If the two-step reduction is correct, there should be two reduction peaks and two oxidation peaks on CV Curves.

With the deepening of research, we find more facts cannot be explained by the "shuttle mechanism". For example, capacity attenuation is directly related to the amount of electrolyte,[8] and sulfur load of cathode has a great impact on cyclic performance. [9] If the redox process of PSs is only the growth and shortening of polysulfide chain, the amount of electrolyte will not affect the performance of cathode. Recently, we found that the redox process of PSs is an electrochemical reaction coupled with chemical process. [10–11] Among them, the disproportionation reaction between PSs and S_8 plays an important role in the process of electrode. The chemical reaction is described as:



In the above formula, forward reaction makes that PSs deposits S_8 on surface of carbon, which leads to the passivation of cathode; Backward reaction makes that S_8 re-dissolves into longer-chain PSs, which causes the activation of the electrode. Multistep reactions between PSs had been studied extensively, [12–13] but there are few studies related to PSs reaction in low dielectric constant solvents like DME/DOL, while it is the main electrolyte solvent of a Li/S battery. In particular, impact of disproportionation reaction lacks sufficient understanding. In this paper, we aim to reveal the influence of disproportionation reaction on electrode process.

2. Experimental Section

2.1 Preparation of electrolyte and electrode

Weighed the required $LiCF_3SO_3$ mass for preparing 1mol/L electrolyte. Baked it at 120°C for 2 hours. Then dissolved in 30ml ethylene glycol dimethyl ether and 1,3 dioxolan mixed solvent (DME/DOL, volume ratio 1:1) to form ether electrolyte.

S/MC (MC: mesoporous carbon) composite cathode: Weighed the required mass of S/MC (S content 50 wt%, MC surface area: $519m^2/g$) and polyvinylidene fluoride (weigh ratio 9:1). Added 1-methyl-2-pyrrolidone after full mixing, Continuously ground to form slurry. Coated evenly on the aluminum sheet with a diameter of 1.3cm, dried at 60°C in vacuum for 2 hours. Two kinds of sulfur loading on the cathode were applied: $1.37mg/cm^2$ and $4.27mg/cm^2$.

2.2 Cell assembly

Coin cell (CR2025) was assembled in a glove box filled with argon. Put the S/MC composite into the bottom shell, dropped the electrolyte, put on a separator, stacked a lithium sheet and a foam nickel, covered the top shell successively. Then the cell was removed from the glove box and sealed with a sealing machine. The volume of electrolyte was about 0.3ml, UBE(Japan) porous film was used as separator.

2.3 Electrochemical Measurements

Galvanostatic charge/discharge performances were carried out in the potential range of 1.5-3.0 V at 25°C using a LAND CT2001A (Wuhan, China), constant current: 60mA/g-S. The cyclic voltammetry at room temperature was tested by three-electrode method on CHI660d (Shanghai, China) electrochemical workstation. Work electrode: S/MC, Reference electrode: silver wire, Counter electrode: aluminum sheet. Scan voltage range: -2.5~+1V vs Ag_2S/Ag , scan rate: 1mV/s. Scanned for 3 cycles. Two kinds of electrolyte volume were applied: 0.3ml and 5ml. AC impedances of coin cell were tested on CHI660d. The spectra was recorded via applying a 5mV voltage perturbation (100 KHz-100 mHz) at open circuit.

3. Results And Discussion

3.1 Passive film on carbon surface

The changes of morphology at the surface of sulfur electrode before and after 1st discharge are compared in Fig. 1. Before discharge, the solid sulfur is closely combined with the carbon matrix. Most of them is encapsulated in the pores of porous carbon. Therefore, only the morphology of spherical porous carbon can be seen from SEM, while the morphology of sulfur can't be seen. After discharge, the surface of carbon electrode is covered by a loose solid layer. The solid layer is mainly composed of spherical solids with large particle size. The composition of solid layer was considered to be Li₂S in previous reports. [14–16] However, it is not supported by dramatic volume change after discharge. The volume of discharge products increases more than tenfold, covering the carbon surface and forming a solid film. The density of sulfur is 2.07g/cm³ while the density of Li₂S is 1.66g/cm³. The solid volume will increase by only 1/5 on assumption that Li₂S generated from sulfur. Nevertheless, the volume of sulfur encapsulated in porous carbon is less than half of the pore volume. If solid product is Li₂S, it is not enough to generate a continuous solid film after discharge. We have confirmed that main component of solid film is S₈. [10] This conclusion can also be understood as follows: Disproportionation reaction is the nature of PSs, and the main product of PSs disproportionation reaction is elemental sulfur. [17] After discharge, most of sulfur encapsulated in carbon pores is dissolved in the electrolyte, and then reprecipitated on the surface of the carbon electrode through disproportionation reaction. That is, sulfur is transferred from the pores to the surface of carbon. This process leads to the formation of a continuous passivation layer on the carbon surface. Another evidence of sulfur production in the later stage of discharge is: the discharge capacity of a Li/S battery is 1254 mAh/g, which is only 3/4 of the theoretical capacity. That is to say, 1/4 of the sulfur cannot be used after discharge. The existence of residual elemental sulfur in the later stage of discharge has been reported. [18] Our previous studies have also proved that the electrode process is an electrochemical reaction accompanied by the disproportionation of PSs to generate S₈. [11] The disproportionation reaction of PSs precipitates elemental sulfur, resulting in the formation of solid film on the electrode.

The solid film of carbon electrode can also be analyzed by Impedance Spectroscopy. The Impedance Spectra of sulfur cathode before and after discharge are compared in Fig. 2. It can be seen that the overall impedance of cathode decreases after discharge. This phenomenon cannot be explained by generation of Li₂S which is also insulating. The decrease of impedance can only be explained by the improvement of cathode conductivity caused by dissolution of sulfur in carbon pores. The arc in the middle frequency band (8.2-176Hz) after discharge is a symbol of film formation. [19]

Equivalent circuits of Impedance Spectrum before and after discharge are shown in Fig. 3. The difference of two circuits is that impedance caused by (R_g CPE2) occurs after discharge, which is indicated by yellow part in Fig. 3. (R_g CPE2) is employed to fit impedance of solid film produced after discharge. The meaning of element in circuits is the same as that in literature [19]. The fitting results fits well with experimental data (shown in Fig. 3.) Detail results are listed in table I.

Table 8 The fitting results according to equivalent circuit

Element	R_e	R_{ct}	CPE1	W	R_g	CPE2
Before discharge	12.69	52.89	2.503×10^{-5}	0.187		
			$n = 0.758$			
After discharge	9.985	6.68	3.63×10^{-5}	0.052	6.852	3.4×10^{-2}
			$n = 0.726$			$n = 0.496$

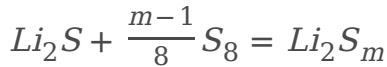
Impedance curves before discharge are composed of one depressed semicircle in high and a slash in low frequency. The intersection of the high-frequency end and the x-axis represents the resistance of the electrolyte (R_e , the fitting value = 12.69 Ohm). The intersection of the low-frequency part and the x-axis represents $R_e + R_{ct}$. R_{ct} : charge transfer resistance, the fitting value = 52.89 Ohm. Depressed semicircle in impedance spectra is the characteristics of porous electrode. After discharge, the Impedance spectra turns into two depressed semicircles followed by a long sloping line. Another depressed semicircle at middle frequency (8.2-176Hz) represents formation of solid film on electrode surface. R_{ct} reduces to 6.68 Ohm. This is because elemental sulfur embedded in carbon pores dissolves into electrolyte during discharge, resulting in increase of conductivity of electrode and concentration of long-chain PSs. R_g represents the resistance of solid film, the fitting value of R_g is 6.852 Ohm. The value is not so high enough that formation of solid film does not block cathodic reaction.

In brief, the discharge process may be as follows: At the beginning of discharge, sulfur in close contact with carbon gets electrons and is reduced to Li_2S . Li_2S reacts with sulfur through solid phase mechanism to form PSs, which is dissolved in electrolyte. During the discharge, most of sulfur is dissolved in electrolyte by reacting with PSs. At the same time, PSs reprecipitates sulfur on surface of cathode through disproportionation reaction to form solid film. The subsequent cathodic process is mainly sulfur dissolution-reprecipitation process.

3.2 The activation of cathode

Cyclic Voltammetry of PSs solution on porous cathode is shown in Fig. 4. Different from the two reduction peaks and one oxidation peak usually reported in previous literature, there is no reduction peak or oxidation peak on curves. The reason is that CVs in previous literature is usually measured with two electrodes, while CVs in Fig. 4 is measured with three electrodes. It is known from the previous study that S_8 is suspended in solution in form of colloidal particles. [11] Therefore, it will also be deposited on surface of cathode. In the (-1~+1V vs $\text{Ag}_2\text{S}/\text{Ag}$) voltage range, the current is very small. The cathode is considered to be passivated because its surface is covered with sulfur. When potential is lower than -1V,

the current increases linearly. According to Impedance results, solid film was covered on cathode surface during sulfur reduction. If the reduction product is Li_2S , its generation will reduce the current rather than increase it for Li_2S is an insulating solid. Possible reason can only be the decrease of sulfur covered area on cathode. The process may be as follows: At the beginning, most of cathode surface is covered with sulfur, so the current is very small. With negative sweep of potential, sulfur in close contact with carbon obtains electrons and is reduced to Li_2S . Li_2S reacts with sulfur to form PSs, thereby is dissolved in electrolyte, resulting in the decrease of sulfur covered area. The reaction is:



The area covered by sulfur decreases, which lead to activation of electrode, therefore the current increases. This process is self-accelerated.

As we all know, the electrochemical reaction rate is much higher than the chemical reaction rate, but when the electrode surface is passivated by chemical reaction products, the whole reaction rate is determined by the chemical reaction rate. The dissolution rate of sulfur due to disproportionation reaction is slow. As can be seen from Fig. 4, the current of 2nd cycle and 3rd cycle is less than that of 1st cycle in the (-1~-2.5V) voltage range. Although PSs undergoes multiple electrochemical-chemical reactions, dominant reaction is the disproportionation reaction between PSs and S_8 .

The electrode in Fig. 5 is the same as that in Fig. 4, except that the volume of electrolyte used is much smaller than that in Fig. 4, which is only 1/20 of that in Fig. 4. The sulfur load is 2.5mg/cm^2 . The overall trend of current in Fig. 5. is similar to Fig. 4, except that current shows wavy twists and turns when potential is lower than -1V (shown in inset circle). The reasons for the wave in current are as follows: When potential sweeps negatively, Li_2S is generated and reacts with S_8 to form PSs. Since volume of electrolyte is small, the concentration of PSs near electrode soon reaches large enough, that is, high concentration and long-chain PSs is produced. The PSs has great solubility in sulfur, so sulfur dissolves into electrolyte, resulting in reduced electrode passivation and increased current. Nevertheless, the disproportionation reaction is nature of PSs. Higher concentration leads to faster generation of sulfur, therefore, electrode passivation becomes heavier and the current decreases.

3.3 Discharge-charge Process

Figure 6 shows 1st discharge-charge curve in a Li/S battery with sulfur load of 1.37mg/cm^2 , which is similar to that reported in usual literature. The discharge-charge process can also be explained by dissolution-reprecipitation mechanism of sulfur. [11] Average chain length of PSs determines the discharge voltage. In discharge platform, average chain length of PSs remains basically unchanged. When the solubility of sulfur changes, the chain length of PSs will change, thereby lead to platform swings. The average chain length of PSs decreases during discharge and increases during charging. PSs is highly unstable, and disproportionation reaction can easily lead to electrode passivation. It is obvious when the sulfur load increases.

Wavy fluctuation can be seen in discharge platform with high sulfur load. Wavy twist is shown by inset circle in Fig. 7. The platform is 1.95V, which is different from the platform (2.05V) in Fig. 6 and usual report of 2.1V. We believe that the small change of platform originates from the change of sulfur solubility in electrolyte, and generation of wavy fluctuation originates from change of sulfur solubility, too. When sulfur load increases, the passivation of the electrode will increase, resulting in the decrease of platform. With the progress of discharge, more short-chain PSs generate, thus the solubility of PSs to sulfur decreases. The steep drop of voltage in the later stage of discharge is due to the quick decrease of sulfur solubility. The reasons for the wave in platform are as follows: When electrode contains more sulfur, the bulk sulfur will dissolve into electrolyte, thereby electrolyte near electrode contains high concentration long-chain PSs. The sulfur dissolution rate on electrode is accelerated, so the electrode is activated and the voltage increases. High concentration PSs can be diluted by bulk electrolyte. When the solubility of PSs to sulfur decreases due to dilution, the sulfur dissolution rate slows down, hence the electrode passivates and the voltage decreases. Results shown above prove that sulfur is dissolved and deposited at all times in discharge cycle. In charging platform, we also observed the wavy fluctuation. Based on the dissolution and deposition of sulfur, we use a novel mechanism to explain the charge discharge curve. [11] It is proved that sulfur dissolution-reprecipitation runs through discharge-charge cycles of a Li/S battery.

4. Conclusion

The kinetic process of cathode in a Li/S battery is an electrochemical process accompanied by chemical equilibrium. Elemental sulfur dissolves and redeposits in forms of PSs through disproportionation reaction at all times in the process of electrode reaction. The carbon electrode is covered by a solid film composed of deposited elemental sulfur after 1st discharge. The dissolution and deposition of sulfur runs through the whole process of battery reaction. Chemical process is obvious when lean electrolyte and high sulfur load are presented.

Declarations

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

All authors have given approval to the final version of the manuscript.

Acknowledgments

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Figures

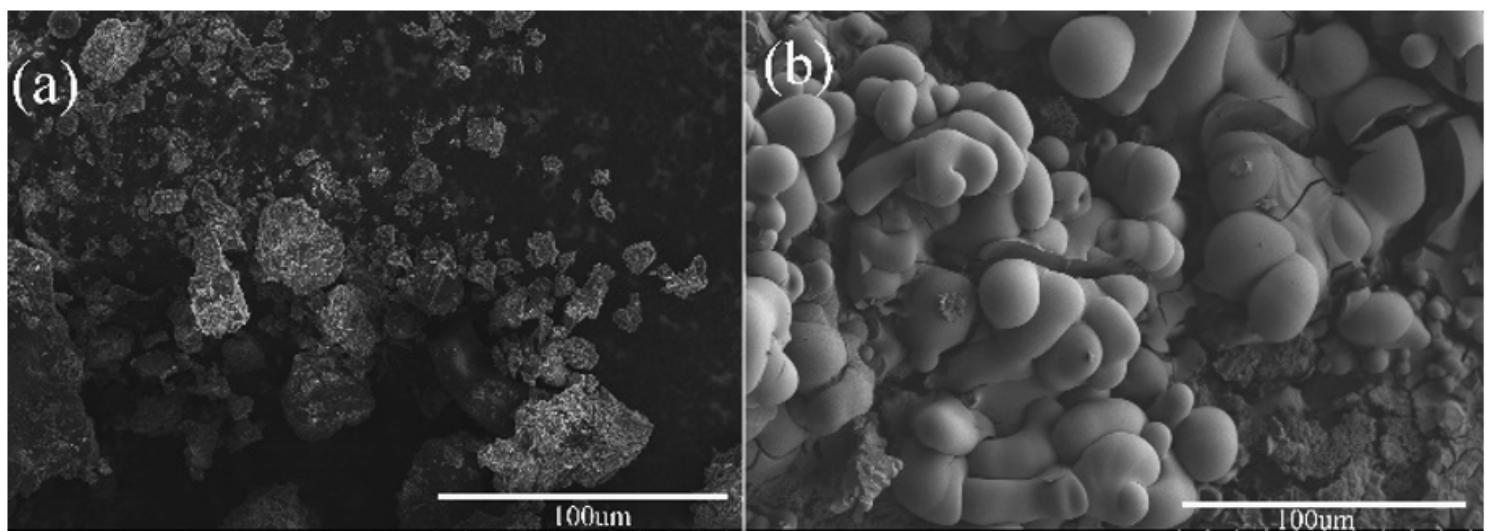


Figure 1

Comparison of morphology at the surface of sulfur cathode (a) freshly assembled (b) after 1st discharge

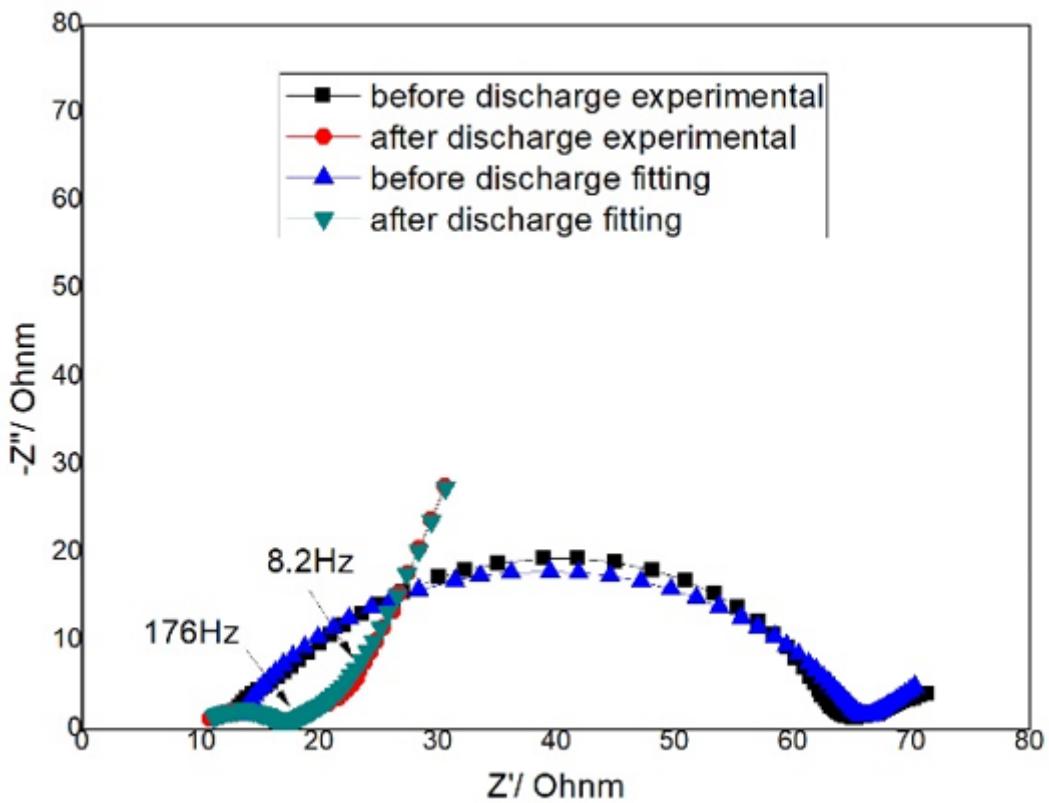


Figure 2

Comparison of Impedance Spectra of sulfur cathode before and after 1st discharge

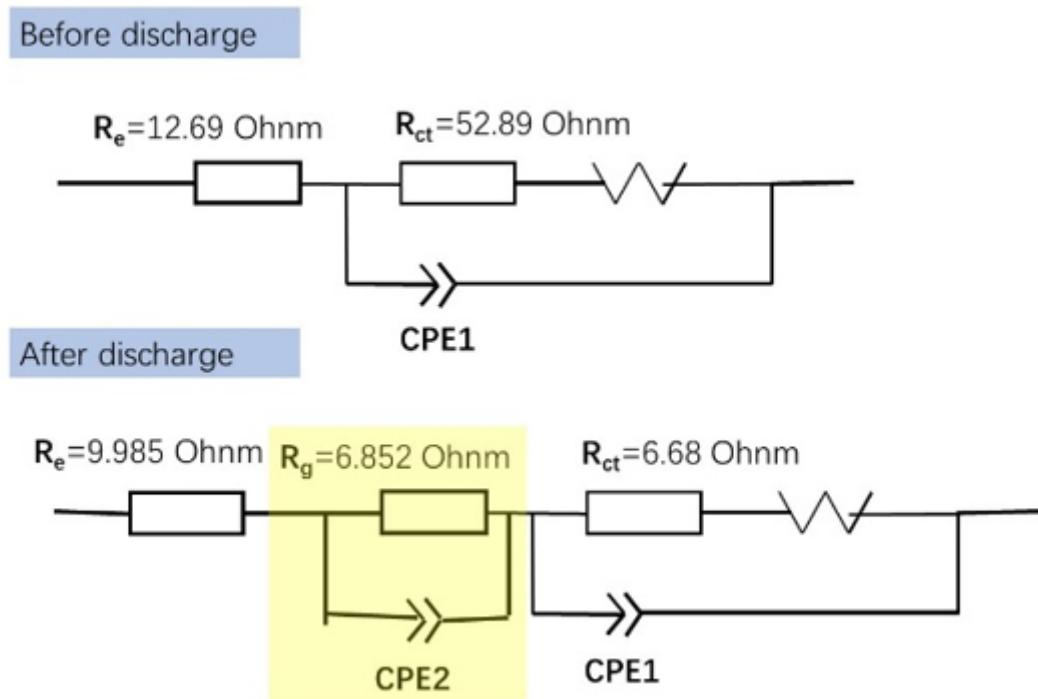


Figure 3

Equivalent circuits of Impedance Spectrum before and after discharge

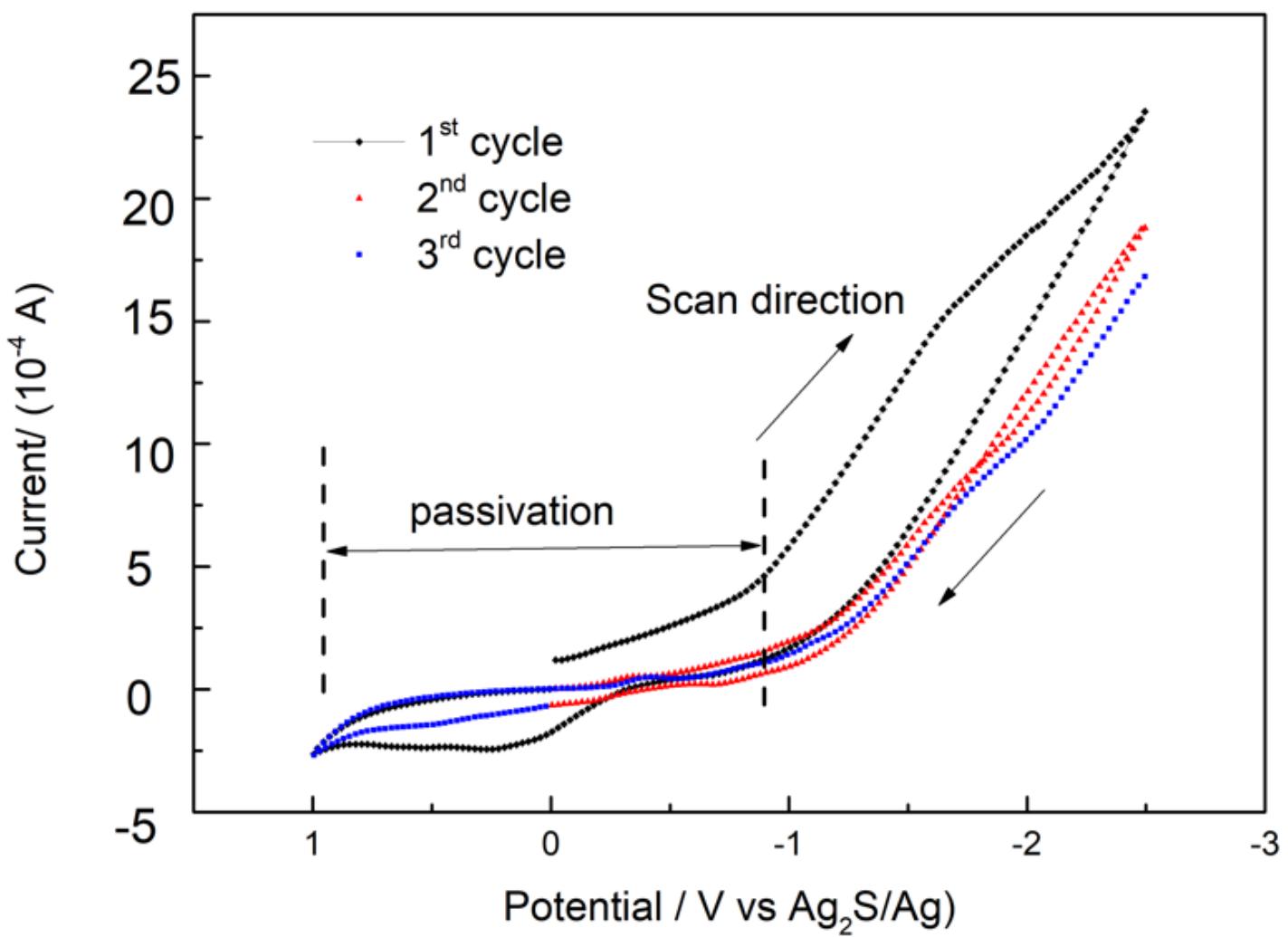


Figure 4

Cyclic voltammetry of Polysulfides on porous carbon (Volume of catholyte: 6ml)

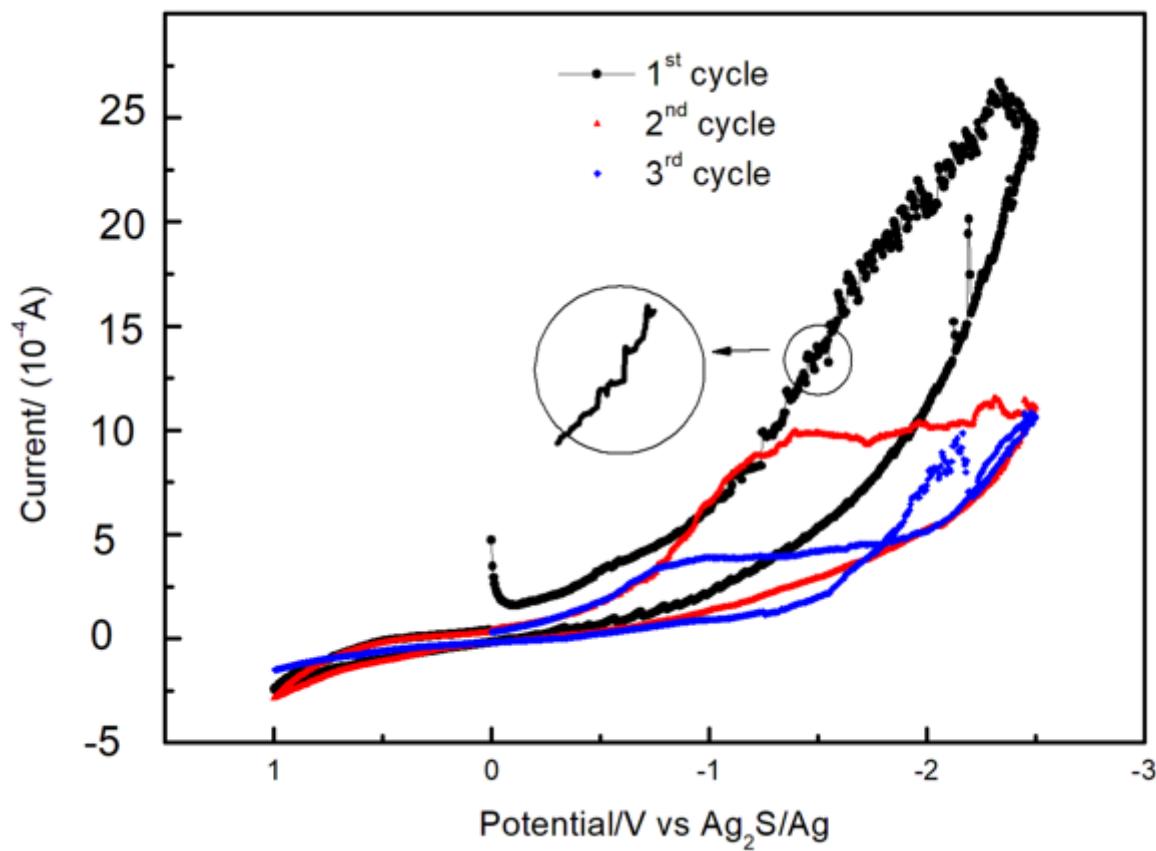


Figure 5

Cyclic voltammetry of Polysulfides on porous carbon (Volume of catholyte: 0.3ml)

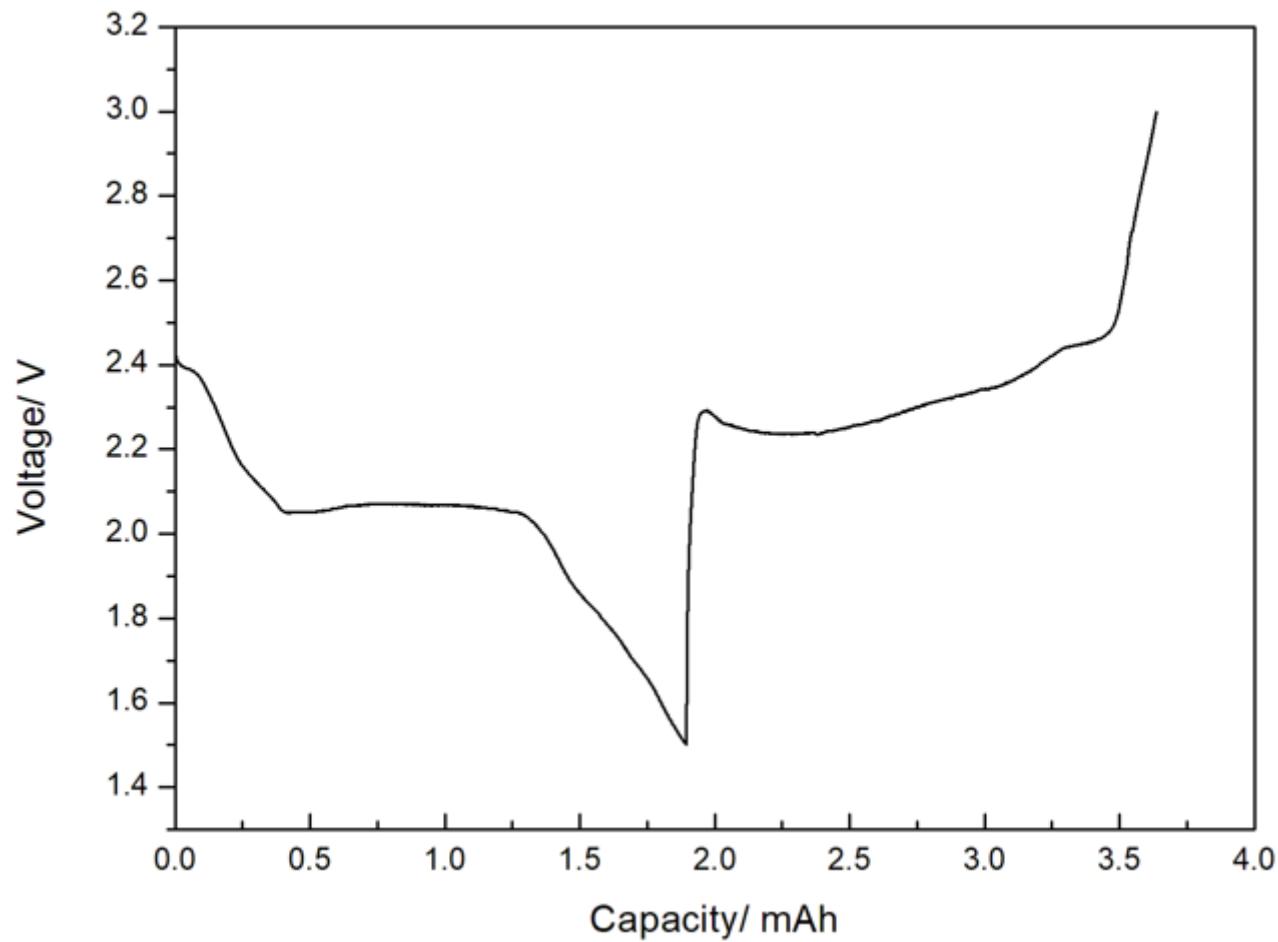


Figure 6

1st discharge-charge curve in a Li/S cell, Sulfur load: 1.38 mg/cm²

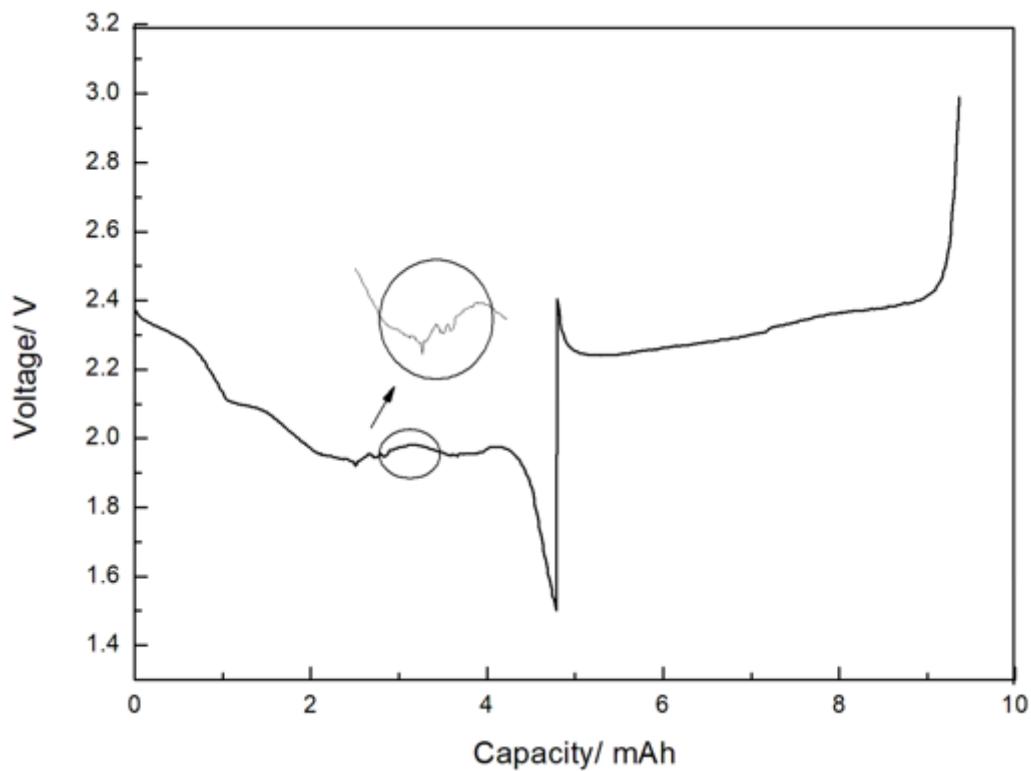


Figure 7

The 1st discharge-charge curve in a Li/S cell, Sulfur load: 4.27mg/cm²