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Experimental investigation of reaction rates during electrodeposition in Li-Sulfur battery

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ABSTRACT: Li-Sulfur battery has garnered attention due to its high energy density. However, owing to complex chemistry the working mechanism is still ambiguous and often contradictory among peers. Here we present an experimental investigation of Li-S battery cells where the behavior of current transient during potentiostatic discharge were studied. It was found that the formation of Li₂S is more likely through electrodeposition rather than chemical deposition. The nucleation and growth rate were measured by assuming a 2D progressive nucleation and growth. The analysis was performed on cells with different electrolyte amount. It was observed that at rapid discharge the rate the growth is limited by mass transfer.

KEY WORDS: Li-Sulfur battery, Nucleation, Electrodeposition, high energy, mechanism, EV.

1. INTRODUCTION

The traction batteries of present day electrified vehicles (EV) are dominated by lithium-ion (Li-ion) battery technologies (1). Due to its comparative high specific energy, power and long lifetime, lithium-ion has undoubtedly surpassed other battery technologies, e.g. Nickel metal hydride (Ni-MH) batteries (2, 3). However, popularity of EVs is still limited compared to traditional internal combustion engine (ICE) vehicles despite of incentives from governments, mainly due to electric driving range limitation and high cost of the battery system. Energy content of battery determines the maximum driving range and gravimetric specific energy is the energy content per unit weight. For instance, Tesla model S is an EV with a driving range of up to 500 km (NEDC) is powered by a battery system with a specific energy of ~260 Wh/kg at cell level. Achieving a driving range higher than 700 km can eventually surpass the popularity of ICE vehicles. To achieve such range, the specific energy of battery cells should be more than 400Wh/kg. Li-Sulfur based batteries have a theoretical specific energy of more than 3000 Wh/kg. Due to such high energy density, Li-S technology has gathered a great attention among academic researchers and industries over the past decade (4). Moreover, the use of inexpensive sulfur can reduce the cost of Li-S battery below 100 €/kWh.

In practical systems however, a Li-S battery cell showed much inferior specific energy. The principal reasons are: 1. need of adding conductive agent e.g. carbon to sulfur to increase its electronic conductivity, 2. Irreversible capacity loss due to insulating discharge product dilithium sulfide (Li₂S), 3. Polysulfide shuttle phenomena; a parasitic reaction of higher order polysulfides (LiSₓ, 8 ≤ x ≥4) at the anode (5). To overcome these limitations, clear understanding of the electrochemistry of the Li-S system is crucial. Although significant insight has been gained through advanced characterization and modelling techniques, the mechanistic understanding of the electrochemistry is still ambiguous (6). Beside high energy, high power is another essential characteristic an EV battery cell should possess. But present Li-S battery cells’ lack high power capability(7) and the number of published studies regarding the power or high current rate capability is low (8). It is reported in the literature that one of the limiting process for capacity at high current rate is the LiS formation (9). However, there are contradicting opinion of the mechanism of Li₂S formation. Some suggested the formation of
Li:S through chemical deposition(10) while others suggested through electrodeposition (11).

In this study we investigate discharge behavior of Li-S battery cells. In particular, the mechanism of Li$_2$S formation. By employing simple potentiostatic discharge, we investigate the transient current response. By fitting with current transient relation of classical electrodeposition we further determine the nucleation and growth rate of Li$_2$S formation.

2. EXPERIMENTAL

3.1. Cell Fabrication

Several Li-S coin cells were fabricated with Cathode containing 50% Sulfur, 40% Carbon and 10% PVDF binder. The loading of sulfur was between 0.9-0.95 mg/cm$^2$. Li metal foils with a thickness of 50 μm were used as anodes. Electrolyte contained ether based solvents and LiTFSI salt of amount 30-50μL. Fabrication process were carried out in a laboratory dry room in CIDETEC.

3.1. Characterization Equipments

Fabricated coin cells here placed in coin cell holder (Bio-Logic CCH-124). Charge discharge and potentiostatic measurement were carried out by Bio-Logic battery tester BCS-805. The voltage window for measurement was 1.7V-2.6V.

3. RESULTS AND DISCUSSION

3.1. Discharge Behavior

During a typical discharge, elemental sulfur in the cathode goes through the following chain reactions. At first the solid S8 converts to liquid S8 by chemical dissolution. After that by electrochemical chain reactions (R2-R6) liquid S8 converts to S2$^-_2$.

\[ S_8(s) \rightarrow S_8(l) \]  
\[ \frac{1}{2}S_8 + e^- \rightarrow \frac{1}{2}S_8^2^- \]  
\[ \frac{3}{2}S_8^2^- + e^- \rightarrow 2S_8^2^- \]  
\[ S_8^2^- + e^- \rightarrow \frac{3}{2}S_4^2^- \]  
\[ \frac{1}{2}S_4^2^- + e^- \rightarrow S_2^2^- \]

From S$^2_2$-, mechanism of formation of Li$_2$S have contradiction among peers. It can either formed through electrochemical reduction to S$^2_-$ and subsequently chemical deposition to Li$_2$S as-

\[ \frac{1}{2}S_2^2^- + e^- \rightarrow S_2^- \]  
\[ 2Li^+ + S_2^- \rightarrow Li_2S \downarrow \]

Or S$^2_2$- can be electrochemically deposited as Li$_2$S as

\[ 2Li^+ + 1/2S^2_- + e^- \rightarrow Li_2S \downarrow \]  

Figure 1 shows a typical discharge voltage profile of a 3 mAh cell at C/10 current rate. The complete voltage profile can be divided in two parts, as shown in figure 1. This division is based on the position of reaction R8 i.e. the electrodeposition reaction. Apparently, at the beginning of Part II, electrodeposition reaction starts and is reflected by a flat voltage region.

![Figure 1: A typical discharge curve of Li-S battery cell at C/10 (C=3mAh).](image1)

Figure 2 shows the voltage profile of a 3 mAh battery cell during discharge at different current rate. Important to notice here, the loss of discharge capacity due to higher current in Part I is insignificant whereas significant reduction in Part II discharge capacity can be seen. This implies that the current rate limitation is dominant in Part II and in particular the electrodeposition reaction (R8).

![Figure 2: Discharge curve of a Li-S cell of 3 mAh at different C rates.](image2)

3.2. Potentiostatic discharge behavior

In order to understand the mechanism and rate of electrodeposition reaction, a series of tests have been performed based on potentiostatic discharge.

The potentiostatic discharge test is divided in 4 stages (see figure 3): i) constant current discharge at C/10 until 2.13 V; this is a voltage until which the electrodeposition reaction either does not start or needs an incubation period of more than 20 hours, ii)
constant voltage discharge at 2.13 V for 2 hours to allow extra time for reduction from high order polysulfide to low order polysulfides, iii) constant voltage discharge at a voltage lower than 2.13 V for 20 h (the difference between this voltage and 2.13 V is the overpotential which drives the electrodeposition reaction), iv) constant current discharge until the end of discharge voltage (1.7 V). The procedure is repeated at different 2.12, 2.11, 2.10, 2.8, 2.4, 2.0 and 1.95 V (step iii). If electrodeposition occurs (here Li$_2$S according to R8), at stage iii, the measured potentiostatic transient current should give an indication of the electrodeposition reaction and its rate (12).

Figure 3: Schematic of a voltage profile of a overpotential discharge test with applied overpotential 0.09 V.

Figure 4 shows the current transient resulting from potentiostatic discharge at different voltages. A general characteristic of the electrodeposition current can be seen in all the profile except at 2.12 V (figure 4a). This implies that, for starting electrodeposition an overpotential of more than 0.01 V is needed for this particular system. Other potentiostatic current profiles have similar pattern. The current shows a sharp drop at the beginning due to double layer capacitance. Then the current increases up to a maximum and falls asymptotically and this behavior is typical for a electrodeposition reaction (12). The position of this maximum varies according to the applied overpotentials. For higher overpotentials the maxima appear sooner in time and larger in magnitude.

Now these potentiostatic transient current can be compared to any classical monolayer electrodeposition, which has similar behavior. And indicates that the electrodeposition of Li$_2$S instead of chemical deposition. Based on this behavior a 2-dimensional nucleation and growth of Li$_2$S can be probable. Following figure 5 shows a schematic of 2D Li$_2$S nucleation and growth. The growth takes place at three phase (Electrolyte, Li$_2$S and Carbon) boundary. As the discharge progresses, the available reactive surface get populated by Li$_2$S. As the conductivity of Li$_2$S is very low, as soon as the reactive area depletes the discharge stops with a sharp voltage drop towards 1.7V.

Figure 5: Schematic of 2D nucleation and growth of Li$_2$S.

Theoretically the current transient, I of a 2D progressive nucleation and growth are expressed as-

$$I(t) = I_m \exp \left[ -\frac{2}{3} \left( \frac{t}{t_m} \right)^{3/2} - \frac{1}{3} \left( \frac{t}{t_m} \right)^{3} \right]$$  \[1\]  

Where, $t_m$ and $I_m$ are the coordinates of current maxima and $t$ is the time of potential perturbation. But this current only represent the electrodeposition Li$_2$S. But as in case of Li-S several electrochemical reactions (R2-R5) precedes the electrodeposition of Li$_2$S (R8), the observed current (figure 4) is a cumulation of all the reaction current. The electrodeposition current can be achieved by subtracting the background by two exponential functions as-
\[ I_b = a_1 \exp(-a_2t) + b_1 \exp(-b_2t) \quad [2] \]

\[ \frac{I}{I_{\text{total}}} = I + I_b \quad [3] \]

Where, \( a \) and \( b \) are constants. Figure shows an example of background fitting of resulting current from the reduction of other polysulfides (R2-R5), \( I_b \). The area marked by red is the area under the fitted current, \( I_b \). Subtracting \( I_b \) from the total current should provide the current from electrodeposition of LiS (R8) only. The subtracted current of electrodeposition then was fitted by equation [1]. Same fitting procedure was repeated for all the potentiostatic discharge current. Curve fitting tool of MATLAB was used for fitting, the average RMSE of the fitting was below 1e-3.

\[ \frac{I}{I_{\text{total}}} = \left( \frac{t - p}{t_{\text{p}}^3} \right) \exp \left[ -\frac{2}{3} \left( \frac{t - p}{t_{\text{p}}^3} \right)^3 - \frac{t}{t_{\text{p}}^3} \right] \quad [4] \]

Where \( p \) accounts for the incubation period.

Figure 6: Subtraction of background (red area) current from electrodeposition current during potentiostatic discharge at 2.08V.

Figure 7: Complete fitting of current transient during potentiostatic discharge at 2.04V.

Figure 7 shows the complete fitting of current transient by equation [1]-[3] for potentiostatic discharge at 2.04V. Important to mention here, potentiostatic discharge at 2.11V (i.e. overpotential 0.02V), the electrodeposition start after long waiting period. This period is known as incubation period as can be see in figure 8. Transient current with such incubation period was fitted by an modified equation as-

\[ t_{\text{m}} = \left( \frac{2}{4\pi A k^2} \right)^{\frac{1}{3}} \quad [5] \]

Where \( A \) is the nucleation rate constant (cm\(^{-2}\)s\(^{-1}\)) and \( k \) is the growth rate (cms\(^{-1}\)). Therefore, the combined nucleation and growth rate constant, \( Ak^2 \) can be determined directly from the location of the potentiostatic current peak. Figure 9 presents the nucleation and growth rate of LiS by electrodeposition. The nucleation and growth rate measurement was carried out for 2 types of cell.

Type-1 (TP1)- 0.9 mg cm\(^{-2}\) sulfur loading in cathode with 50µL electrolyte.

Type-2 (TP2)- 0.9 mg cm\(^{-2}\) sulfur loading in cathode with 30µL electrolyte.
Figure 9: Combined nucleation-growth rate constants obtained from potentiostatic discharge current maxima for two types of cells, TP1-0.9 mg cm\(^{-2}\) sulfur/50\(\mu\)L electrolyte, TP2-0.9 mg cm\(^{-2}\) sulfur/30\(\mu\)L electrolyte.

As can be seen from figure 9 the nucleation and growth rate constant increases significantly in between 2.11V and 2.08V, 4 order of magnitude while between large gap 2.08V to 1.95V the rate only increases only 3 order. This can be explained by dominant transport phenomenon. At low voltage potentiostatic discharge or high overpotential the growth is more controlled by mass transport. High overpotential of potentiostatic discharge is analogous to high current in case of galvanostatic discharge. The mass transport limitation at high current rate is further clarified by the TP2 cell behavior compared to TP1. At high overpotential or low voltage discharge (such as 2.04V, 2.0V, 1.95V), the nucleation and growth rate is inferior in case of TP2 cell. As the amount of electrolyte is low in TP2 cells, the mass transport limitation at high overpotential is comparatively more pronounced. This behavior is crucial in case of fabrication of large cell. In general, the ratio of active material to electrolyte amount should be very high to achieve commercial viability.

4. CONCLUSION

Current transient response during potentiostatic discharge at different voltage or overpotentials of Li-S cell were studied. The current profile can be fitted with theoretical 2D nucleation and growth profile. Which gave the indication of Li\(_2\)S formation through electrodeposition rather than chemical deposition. The combined nucleation and growth rate was also calculated from the current transient maxima. At high current rate or high overpotential the growth is limited by mass transport. It is more evident in cells with low electrolyte amount. These findings can help in developing material to achieve higher capacity at high current rate.

5. FUTURE WORK

In future the potentiostatic discharge tests will also be performed at cells with different cathode loading and at different temperatures. A detailed analysis will be carried out by continuum models.

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