

The mechanism of electrochemical reduction of lithium polysulfides in lithium-sulfur cells

Kolosnitsyn V.S., Kuzmina E.V., Karaseva E.V.

Institution of the Russian Academy of Sciences
Institute of Organic Chemistry of Ufa Scientific Centre
of the RAS

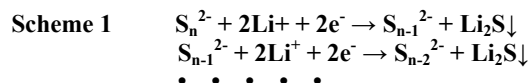
prosp. Oktyabrya, 71, Ufa, 450054, Russia

e-mail: kolos@anrb.ru, elchem@anrb.ru

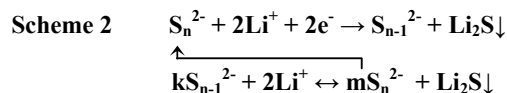
The mechanisms of electrochemical reduction of lithium polysulfides (Li_2S_n) attract interest in connection with the development of lithium-sulfur (Li-S) batteries. The depth of reduction of lithium polysulfides determines the efficiency of sulfur utilization. During the cycling of lithium-sulfur cells highly concentrated solutions of lithium polysulfide are formed.

The electrochemical reduction of lithium polysulfides can be realized by two ways:

- the concentration of lithium polysulfides is kept constant but the length of polysulfide chain (n) is gradually decreased (scheme 1):



- the length of the polysulfide chain is constant due to reactions of disproportionation of lithium polysulfides. The concentration of lithium polysulfides is gradually decreased (scheme 2):



where: $k \cdot (n-1) = m \cdot (n+1)$

In the first Scheme step changes in the open circuit voltage (OCV) as the cell is been discharging should be observed. These should correlate with the oxidation-reduction potential of each of the forms of lithium polysulfides. In the second Scheme the open circuit voltage should gradually decrease.

In reality the mechanism of lithium polysulfide reduction can be more complex. It is likely that it will depend on the system composition and the conditions of cycling [1].

To estimate the most likely mechanism of the electrochemical processes that occur in Li-S cells, we have investigated of the form of the discharge curves of the lithium-sulfur cells by Galvanostatic Intermittent Titration Technique (GITT) [2-3].

The profiles of the discharge voltage and the open-circuit voltage with state of charge are similar, but they have some differences (Fig.). In both profiles two plateaus can be observed that corresponds to the reduction of sulfur and lithium polysulfides, respectively. It should be noted that the «potential dips» between plateaus and also between arched sections of plateau correspond to lithium polysulfides reduction are not observed in the OCV profile (Fig.). This fact indicates that observed «potential dips» are due to cell polarization.

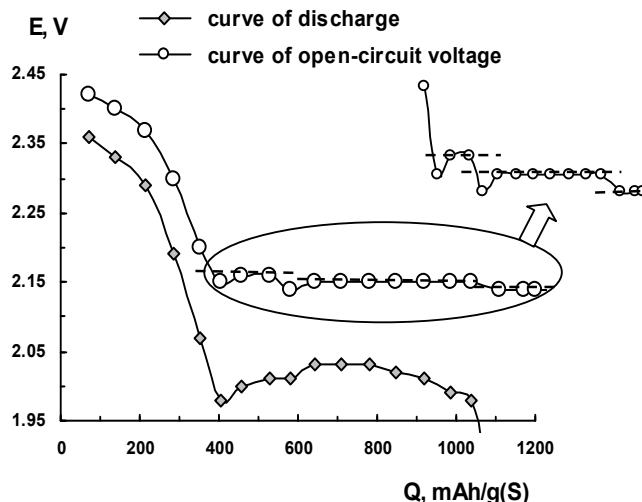


Fig. Profiles of the discharge voltage and the open-circuit voltage of lithium-sulfur cell, obtained by Galvanostatic Intermittent Titration Technique (1st cycle).

$i_{\text{discharge}} = 0,3 \text{ mA/cm}^2$, $t = +30 \text{ }^\circ\text{C}$.

In addition, the polarization of the cell during the first plateau is significantly lower than during the second plateau. The steps on the second plateau of the OCV profile could indicate the presence of the mechanism shown in Scheme 1.

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References

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