

### An investigation of the mechanism of electrochemical reduction of sulfur in lithium-sulfur cells

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The electrochemical reduction of sulfur in lithium-sulfur (Li-S) cells occurs in several stages. The complex shape of discharge curves of Li-S cells reveals information on this. The mechanism of electrochemical reduction of sulfur is poorly understood.

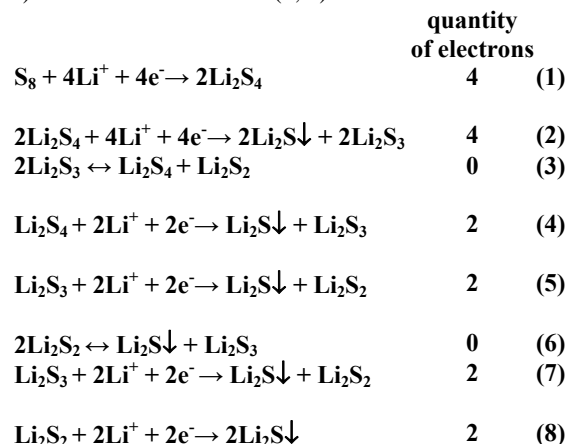
To deduce the most likely mechanism of electrochemical processes that occur in Li-S cells we studied the profiles of the charge and discharge curves of the Li-S cell during long cycling using a method of low-current cyclic galvanostatic polarization.

Two plateaus are observed on discharge curves (Fig. a). The first plateau is at a high-voltage region (2.4 V) and the second occurs at a lower voltage region (2.1-2.2 V). The high-voltage plateau corresponds to sulfur reduction to lithium polysulfides and the low-voltage plateau is due to the reduction of lithium polysulfides to lithium sulfide.

The low-voltage plateau of the discharge curve has complex shape (Fig. b). It consists of two clearly defined arched sections. At the same time there are poorly defined breaks at the each arched part. It should be noted that the «potential dips» are observed between plateaus correspond to sulfur and lithium polysulfides reduction and also between the arched sections of low-

voltage plateau.

The drop shape of low-voltage plateau and the appearance of arches and breaks provide evidence of step-by-step nature of electrochemical reduction of lithium polysulfides. On the basis of shape analysis of the discharge curve we suggested the following process scheme that includes both electrochemical (1, 2, 4, 5, 7, 8) and chemical reactions (3, 6):



According to the suggested process scheme the electrochemical reduction of sulfur occurs by a step-by-step in consecutive reducing of the polysulfide chain length of generated lithium polysulfides and formation of lithium sulfide. Overall this results in the generation of six molecules of lithium sulfide and one molecule of lithium disulfide corresponding to discharge capacity of 1466 mA·h/g(S), which correlates well with experimental data.

This work was supported by Oxis Energy Ltd. (UK) under contract no. 17141/6-07.

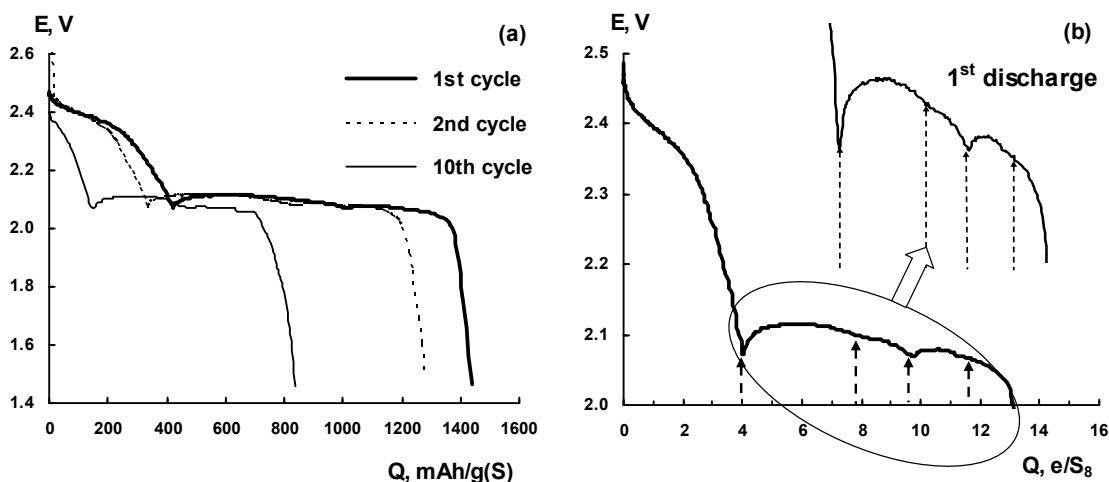


Fig. Discharge curves of lithium-sulfur cells.  $i_{\text{discharge}} = 0,018 \text{ mA/cm}^2$ ,  $t = +30 \text{ }^\circ\text{C}$ .