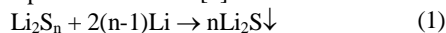


Dilatometric study of lithium electrode during its cycling in electrolyte containing lithium polysulfides

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Usage of metallic lithium as an active material of negative electrode in lithium batteries attracts great interest. However the metallic lithium is not capable to long-term cycling because “dead lithium” generates and accumulates on its surface [1]. The promising electrochemical system with metallic lithium is the system Li-S. During the electrochemical charge and discharge of Li-S batteries intermediate products - lithium polysulfides (Li_2S_n) - are generated. They are sufficiently strong oxidants and can dissolve fine-dispersed precipitates of lithium [2].



The dissolution of fine-dispersed metallic lithium allows to recover “dead lithium” to electrochemical process. It leads to an increase in the cycle life of lithium electrode and safety of lithium batteries. Electrochemical dilatometry is convenient method to study of generation of fine-dispersed lithium.

The aim of this work was to study the volumetric changes of lithium electrodes during galvanostatic cycling in sulfolane electrolyte system containing lithium polysulfides (0.4M Li_2S_6).

The investigations were carried out in special designed sealed stainless-steel cells with plane-parallel electrodes and equipped by dilatometric sensor. Working and auxiliary lithium electrodes were made from lithium foil with thickness 100 μm . Two layers of micro porous membrane Celgard®3501 were used as a separator. Electrode block was pressed at 1 kg/cm^2 . 1M LiClO_4 in sulfolane and 0.4 Li_2S_6 + 1M LiClO_4 in sulfolane were used as electrolytes.

The obtained results (fig. a) show that thickness of electrode blocks are constant at the initial cycles (1÷11). It indicates that fine-dispersed lithium is not generated. In the sequel the thickness of electrode block increases. The velocity of thickness increasing is about 6.5 μm per cycle for 1M LiClO_4 in sulfolane and it is about 3.7 μm per cycle for 1M LiClO_4 + 0.4M Li_2S_6 in sulfolane.

The increase of thickness of electrode block can be explained by the accumulation of “dead lithium” and products of destruction of electrolyte system on the surface of lithium electrodes.

Postmortem analysis of cycled cells showed that separators did not contain liquid electrolyte and there were porous grey layers on the surface of lithium electrodes. Each lithium electrode (working and auxiliary) increased its volume by 55-60 μm .

The initial increase of Li electrodes thickness (fig. a) does not effect to overvoltage of electrochemical reactions during cycling (fig. b). Dramatic increase of

overvoltage occurs at the final stages of cycling when thickness of electrode blocks increased by 70-80 μm .

In the presence of lithium polysulfides the rate of accumulation of “dead lithium” decreases in two times (fig. a) and cycle life increases in 1.5 times (fig. b) in comparison to electrolyte without lithium polysulfides. Obtained data proves the possibility of lithium polysulfides to dissolve the fine-dispersed precipitates of lithium.

It should be noted that in the experimental conditions the lithium polysulfides is used up during cycling of lithium electrodes (1). They are constantly regenerated during cycling of lithium sulfur cells therefore the positive effect of lithium polysulfides on the cycle life of lithium electrodes must be bigger than in “Li-Li” half-cell.

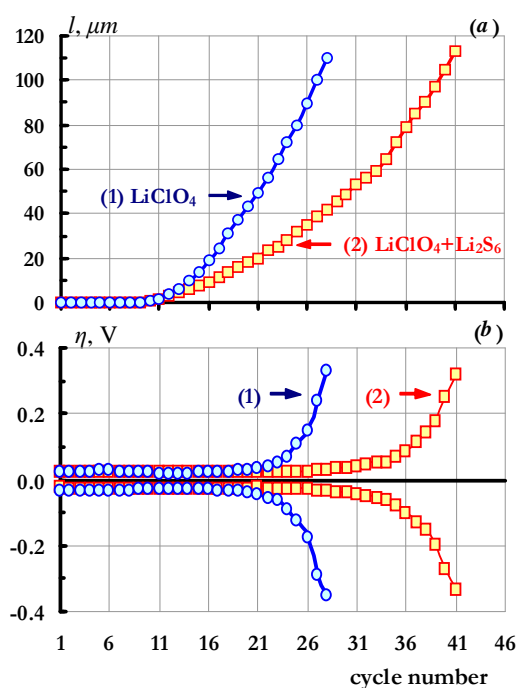


Fig. Dependences of thickness of “Li-Li” half-cells (a) and overvoltage of cathodic and anodic reactions of the lithium electrodes (b) on the cycle number in electrolyte: 1M LiClO_4 in sulfolane (1) and 0.4M Li_2S_6 + 1M LiClO_4 in sulfolane (2).
Deposition/dissolution capacity = 1.0 mAh/cm^2 ;
Deposition/dissolution current density = 0.25 mA/cm^2 ;
Temperature = 30 $^\circ\text{C}$.

Literature

1. Kang Xu. Chemical Reviews, 2004, 104, 4303.
2. Kolosnitsyn V.S., Karaseva E.V., Ivanov A.L. Russian Journal of Electrochemistry, 2008, 44 (5), 564.