

On reasons of capacity fade of lithium-sulfur cells during cycling

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Lithium-sulfur (Li-S) cells have a number of advantages compared to lithium-ion cells: high specific energy, internal mechanism of overcharge protection, wider temperature range, inexpensive and easily available electrode materials as well as environmental safety [1-2]. However despite of their advantages Li-S rechargeable batteries are far from being a commercial success. The main reason for that is the fast capacity decrease during its cycle life. We believe that the capacity degradation of Li-S cell can be caused by the following reasons:

- sulfur is transferred from positive electrode to negative lithium electrode and is accumulated on the electrode surface in form of Li_2S , a final product of sulfur reduction;
- sulfur is encapsulated into micro-pores of carbon structure of positive electrode;
- sulfonation of solvent molecules of the electrolyte system.

The aim of this work was to investigate into the distribution of lithium sulfide between the components of discharged Li-S cells (electrodes and electrolyte) depending on the charge – discharge cycle number

The content of sulfidic sulfur was determined by precipitating potentiometric titration. We used lead nitrate as a titrant. Sulfide ion electrode and saturated chloride silver electrode were used.

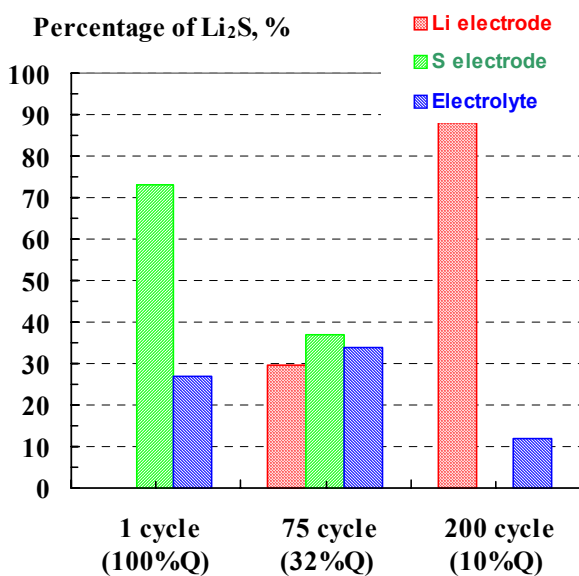


Fig. 1. The distribution of sulfide sulfur between the components of the fully discharged lithium-sulfur cell after different number of charge-discharge cycles.

Q – discharge capacity of lithium-sulfur cell at first cycle.

Fig. 1 shows that during the cycle life a part of sulfur (in form Li_2S) is transferred to the negative lithium electrode and is accumulated on it, another part stays in the electrolyte. It is likely that this part of sulfur is present in the electrolyte in form of lithium polysulfides that have not been electrochemically reduced. As the number of cycles increases the amount of sulfur in the sulfur electrode goes down.

It should be noted that the detected quantity of lithium sulfide decreases during cycling (Fig. 2). This fact can indicate that sulfur is likely to be removed from the field of electrochemical reaction by becoming encapsulated in micro-pores of the carbon structure of positive electrode in the form of molecular sulfur, which can not be determined by using this analytical method.

Therefore the results of this work draw us to conclusion that during cycling sulfur is being transferred from positive to the negative electrode and is accumulated on it in form of lithium sulfide. However this fact cannot be considered as the main reason for the capacity fade of Li-S cell.

A more likely reason for capacity degradation is the encapsulation of sulfur in the micro-pores of carbon structure of the sulfur electrode.

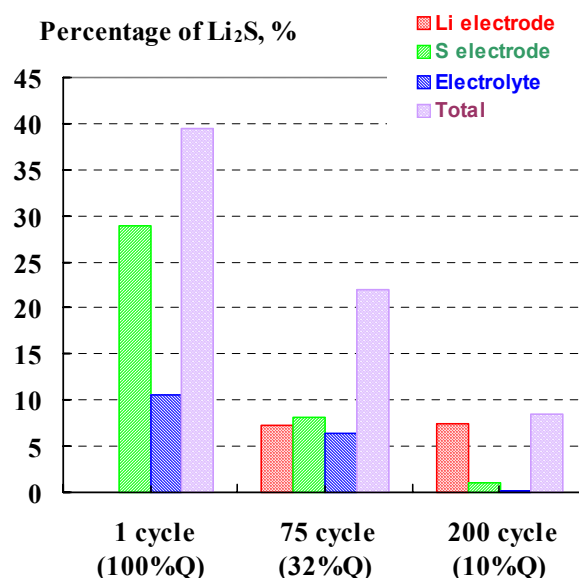


Fig. 2. Proportion found sulfide sulfur of total sulfur in the lithium-sulfur cell.

Q – discharge capacity of lithium-sulphur cell at first cycle.

Reference:

1. S. Kim, Y. Jung, S.J. Park. *Electrochemical Acta*, 2007, **52**, 2116-2122;
2. W. Zheng, X.G. Hu, C.F. Zhang, *Electrochemical and Solid-State Letters*, 2006, **9**(7), A364-A367