Abs. 442, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Charge Efficiency and Self-Discharge Study in Rechargeable Li/S Batteries

Yuriy V. Mikhaylik*, James R. Akridge
Sion Power Corporation
9062 South Rita Road, Tucson, Arizona 85747-9108 USA
*yuriy.mikhaylik@sionpower.com

This work was focused on the development of low self-discharge and high charge efficiency Li/S rechargeable cells with high specific energy. Gibbs energy of the Li/S reaction is more than five times the theoretical energy of a Li-ion system. High reactivity of metallic Li with soluble polysulfides creates an electrochemical shuttle and leads to poor charge efficiency (CE) and high self-discharge (SD). This work presents experimental data showing that lithium protection leads to elimination of the polysulfide shuttle at high charge plateau and as a result significant improvement of charge efficiency and reduction of self-discharge occurs.

Experiments with varying degrees of lithium protection has been conducted with cells containing 1 g of elemental sulfur incorporated into a carbon cathode and 1.2 g of Li foil. Cells weight was ~ 10 g and discharge capacity was in the range of 800–1200 mAh and depended on the degree of lithium protection. Fig.1,2,3 represent cycled cells charge-discharge profiles and discharge profiles after 48 h storage (self-discharge) at charge conditions. Fig.1,2,3 clearly show that lithium anode protection lead to higher charge efficiency and voltage charge termination. As a result of higher charge efficiency sulfur specific capacity increased from 800 to 1200 mAh/g (Fig.3) mainly due to gaining capacity at the high discharge plateau. Self-discharge for these strongly protected cells did not exceed 4% per month. Experimental data show that there is no linear correlation between charge efficiency and self-discharge for Li/S system (Fig.4). Starting charge efficiency increase leads to higher self-discharge (points A to B, Fig.4), than SD stabilization (points B-C) and eventually to dramatic SD reduction at very high charge efficiency (points C-D). Theoretical analysis showed that such complex relationships are connected with the shuttle phenomenon.

Theoretical analysis of the shuttle phenomenon has been done based on the shuttle equation:

$$\frac{d[S_H]}{dt} = \frac{I}{q_H} - k_s[S_H] \qquad (1)$$

$[S_H]$ is a high plateau polysulfide concentration, t is time, I is charge or discharge current, q_H is the sulfur specific capacity related to high voltage plateau and k_S is the heterogeneous reaction constant of polysulfides with the lithium (shuttle constant). The shuttle equation has been applied for charge (positive current), discharge (negative current) and cell storage conditions (zero current). It has been shown that charge efficiency and self-discharge are directly connected for Li/S rechargeable system. Based on the shuttle equation SD vs CE has been simulated (Fig.4) and showed good agreement with experimental data. Analysis of the charge conditions leading to sharp voltage increase (Fig.2, 3) or voltage leveling (Fig.1) allowed development of voltage charge termination criteria as well.

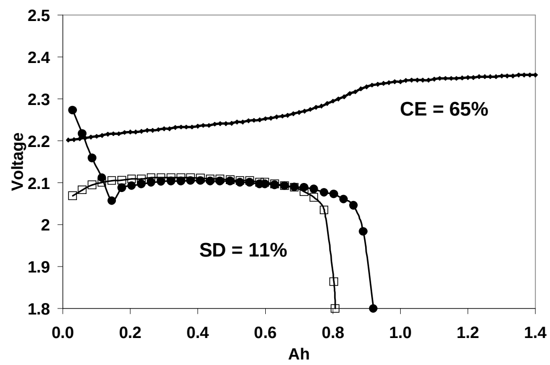

Fig.1. Charge, discharge and discharge after storage profiles for cells with unprotected lithium.

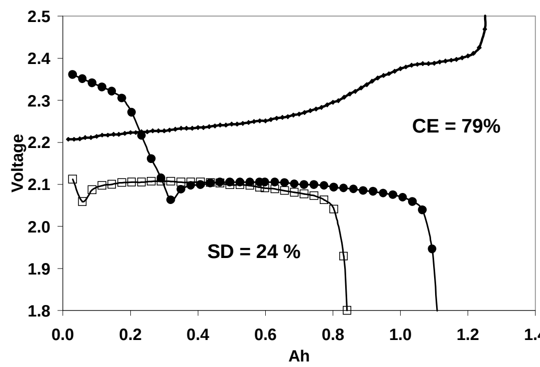

Fig.2. Charge, discharge and discharge after storage profiles for cells with low lithium protection.

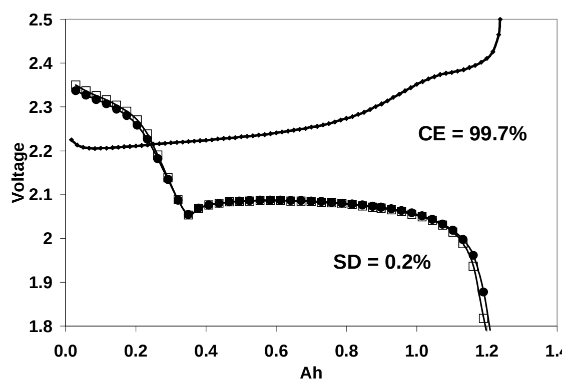

Fig.3. Charge, discharge and discharge after storage profiles for cells with strong lithium protection.

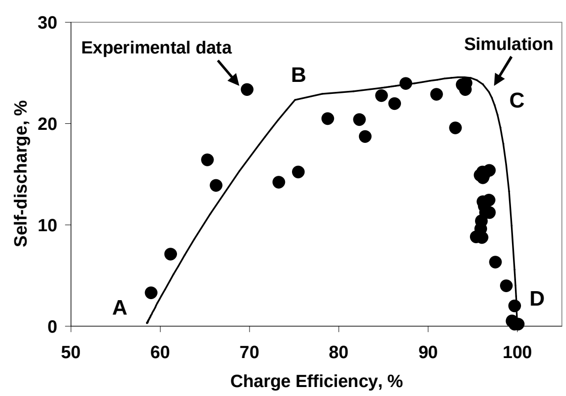

Fig.4. Self-discharge vs charge efficiency. Simulated and experimental data.