

ELECTROCHEMISTRY OF A NONAQUEOUS LITHIUM/SULFUR CELL

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Summary

The development and the electrochemistry of low-rate laboratory prototype Li/S button cells is described. The cell consists of a lithium anode, a porous catalytic current collector which is loaded with sulfur, and an organic solvent containing lithium polysulfide. The case of the cell was made from stainless steel and sealing was accomplished by the use of a combination of organic elastomer and cement (with no crimp). After 3 weeks storage at 60 °C, the button cells lost only about 1 mg of weight. The lithium polysulfide reacts with the Li anode to form a passivating layer which acts as a solid electrolyte interphase (SEI). The e.m.f. of the cells changes from 2.38 to 2.15 V depending on the composition of the solutions. Cells exhibit flat discharge curves at low drains. The energy density of the cells is 730 W h/kg or 900 W h/l at room temperature and 950 W h/kg or 1200 W h/l at 60 °C (calculated on the basis of all cell components, excluding the case). Storage and discharge tests at 60 °C show a capacity loss of 2 - 5% per month depending on solution composition. This indicates a shelf life of at least 10 years at room temperature.

Introduction

The Li-S couple has one of the highest theoretical energy densities, about 2600 W h/kg. This value is greater by 150% than that of Li/MnO₂ and greater by about 70% than that of Li/SOCl₂ cells. In addition, the reaction between lithium and sulfur is reversible so that this system potentially can be developed into a secondary battery [1 - 3]. Because of these advantages the Li-S couple has attracted considerable interest.

Previous attempts to develop Li-S batteries encountered several problems. The first was the incompatibility of lithium with solution components. Lithium reacts with some solvents and with some electrolytes. The most severe problem was its reaction with soluble sulfur. On partial reduction of the solid sulfur at the cathode, polysulfide is formed. This escapes from the cathode into solution and reacts with the lithium leading to its fast corrosion [4].

The second problem was the incomplete reduction of sulfur. For instance, in DMSO [5] (Dimethyl sulfoxide) the sulfur can be reduced only to S_4^{2-} , namely, the maximum efficiency is 25%. In DMAC [6] (Dimethylacetamide) the sulfur or the polysulfide can be reduced to S_2^{2-} , namely, a maximum efficiency of 50%. High efficiency (about 100% at 50 °C) for the reduction of polysulfide in THF was found later by Rauh *et al.* at EIC Laboratories [2].

The third problem was the low conductivity of the organic solutions which contain high concentrations of polysulfides. Elemental sulfur is only slightly soluble in many organic solvents. However, polysulfides are very soluble. For instance, sulfur can be dissolved as polysulfide in THF to a concentration of about 20 mol/liter. Organic solutions containing such a high concentration of sulfur are very viscous and therefore have very low conductivity.

Lithium metal is thermodynamically unstable in THF [7]. However, its relative stability in THF solution is a kinetic phenomenon which depends on the properties of the corrosion product [3]. When the product is insoluble in solution, it precipitates on the lithium to form a passivating layer which prevents further contact of lithium with the solution. An ideal passivating layer for battery systems is the one which has the properties of a solid electrolyte interphase (in short, SEI), namely, a good ionic conductor and good electronic insulator [8]. It was recently found that the corrosion of lithium in THF-polysulfide solution can be decreased by increasing the concentration of the polysulfide and by shortening its chain length [3].

This work describes the development and the electrochemistry of a low-rate laboratory prototype lithium/sulfur button cell in solutions containing THF and toluene.

Experimental

All solutions were prepared and cells were assembled inside an argon filled glove box. THF and toluene (Merck pro analyze) were dried by activated Al_2O_3 . BDH sublimed sulphur was vacuum dried at 80 °C for 24 h. $LiClO_4$ (Fluke purum) was vacuum dried at 150 °C for 24 h. As test vehicles we used laboratory prototype button cells consisting of a stainless steel can. The anode was made from Foote high purity lithium ribbons. The cathodic current collector was a Teflon-bonded carbon, porous electrode supported by Ni Exmet. It was charged with elemental sulfur or polysulfide. Celegard porous polypropylene or glass paper was used as separators. The cell had an internal volume of 0.6 - 0.9 cm^3 and the electrode area was 2.5 cm^2 . It has a nominal energy density of 900 - 1400 W h/l (calculated on the basis of all cell components, excluding the case). Sealing was accomplished by the use of a combination of organic elastomer and cement. After 3 weeks storage at 60 °C the button cells lost only about 1 mg of weight. Lithium corrosion rates were measured at 60 °C using both sealed glass ampoules containing lithium and electrolyte, and button cells. Lithium foil of known weight and

surface area was stored in THF solutions for 7 weeks at 60 °C. After this period of storage the lithium and the sulfide were analyzed quantitatively by acid–base titration and iodometrically.

Results and discussion

Lithium metal is very reactive in THF solution containing elemental sulfur, forming polysulfides. The Li corrosion rate in a saturated solution of sulfur in THF (about 0.3M) was 130 mA/cm² [3]. As the average polysulfide chain length shortened, the Li corrosion rate decreased. When the solution reached the composition Li₂S_{6.6} the average corrosion rate had fallen by about 5 orders of magnitude [3]. This behaviour can be easily understood by the use of the passivating layer model. As long as elemental sulfur is present in solution, the Li corrosion product – Li₂S will dissolve to form polysulfide, and Li will continue to corrode. As the chain length of the polysulfide is shortened, the solubility of Li₂S in the solution decreases and so a sufficiently thick passivating layer can be formed and the lithium corrosion rate decreased.

Figure 1 shows the conductivity of THF solutions *versus* sulfur concentration. The sulfur is dissolved as soluble polysulfide with one mol/liter of LiClO₄ and also without the LiClO₄. The energy densities per unit volume that can be achieved from these quantities of sulfur were calculated on the basis of the prototype button cell which was described above. It can be seen that the conductivity of the solution decreased as the sulfur concentration increased. The rapid decrease in conductivity of the perchlorate solution is a result of the increased viscosity of the solution. In order to reduce the viscosity of lithium polysulfide–THF solution and to increase its conductivity, toluene is added as a co-solvent. As a result, the solubility of the polysulfide and the viscosity of the solution decreased. The conductivity of a saturated solution of polysulfide (*ca.* 0.3M Li₂S₈) in THF:toluene 1:1 by volume, containing 1M LiClO₄, is 1.0 mMho cm⁻¹, about 20 times that of a concentrated solution of polysulfide in THF (containing 1M LiClO₄).

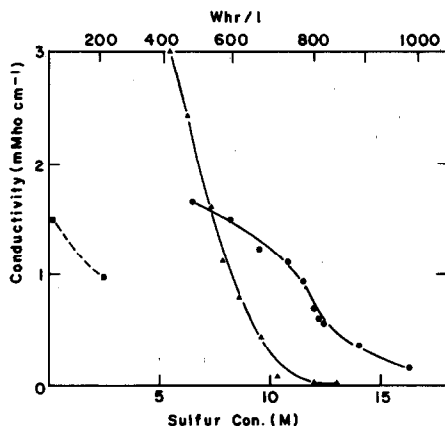
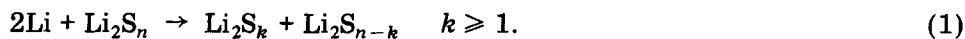


Fig. 1. Plot of the conductivity of THF solutions *vs.* sulfur concentration as soluble Li₂S_{8.4}. ▲, 1M LiClO₄; ●, without LiClO₄; ■, 1:1 toluene:THF, 1M LiClO₄.

Lithium reacts with polysulfide to form either two shorter polysulfides or, when $k = 1$, Li_2S and a shorter polysulfide



The e.m.f. of the cells containing THF as the sole solvent changes with the solution composition and with the length of polysulfide. At 0.9M Li_2S_8 the e.m.f. is 2.38 V. During discharge, the average polysulfide length decreases and the e.m.f. falls. The e.m.f. reached a constant value when the apparent average polysulfide length fell below $\text{Li}_2\text{S}_{5.2}$. When toluene is added to form a 1:1 volume mixture the e.m.f. of the cell is constant — 2.22 V, independent of the state of discharge. The e.m.f. is 2.21 at 1:3 volume ratio of THF:toluene. The change of the e.m.f. with solution composition may be due to the difference in redox potentials of the various polysulfides.

Figure 2 shows a discharge curve of a button cell having an energy density of 730 W h/kg or 900 W h/l (calculated on the basis of all cell components, excluding the case). The solution was 1:1 toluene:THF, 1M LiClO_4 saturated with polysulfide. The cell was discharged for 7 months at decreasing load starting from 2.4 k Ω and ending with 100 k Ω . The sulfur utilization to a cut off voltage of 1.5 was 95%.

Figure 3 shows the discharge curve of a Li-S button cell having the same energy density. The solution was a mixture of 1:3 THF:toluene, 1M LiClO_4 saturated with polysulfide. The cell was discharged through 10 and 22 k Ω loads. The sulfur utilization to a cut off voltage of 1.5 was above 95%. The minimum in the cell voltage is typical of the button cells containing 1:3 THF:toluene. It disappears when the cell is discharged through 60 k Ω or more.

A button cell having a nominal energy density of 1130 W h/kg or 1400 W h/l was stored at 60 °C for 4 weeks. After this period, the cell was discharged through a 22 k Ω load at room temperature to about 10% of its capacity, followed by discharge through 10 and 22 k Ω loads at 60 °C for 5 months (Fig. 4). The cell delivered 86% of its nominal capacity, *i.e.*, 950

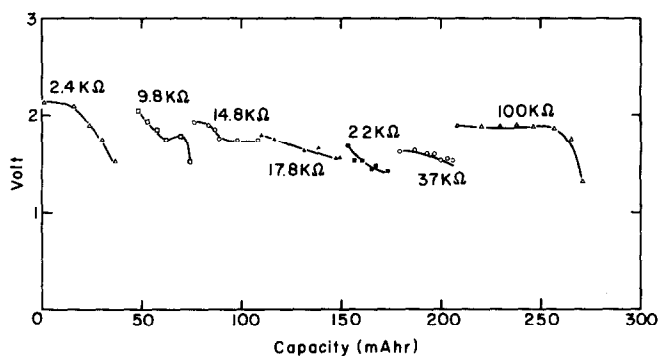


Fig. 2. Discharge curve of a 730 W h/kg button cell. Solution composition:- 1:1 toluene:THF, 1M LiClO_4 saturated with polysulfide.

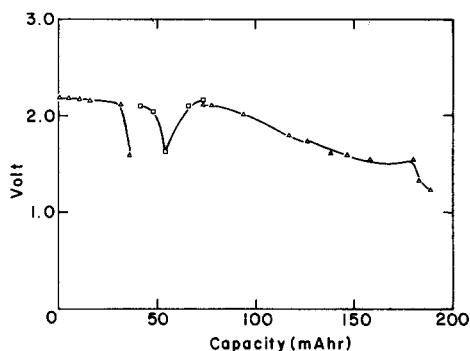


Fig. 3. Discharge curve of a 730 W h/kg button cell. Solution composition:- 1:3 THF: toluene, 1M LiClO₄ saturated with polysulfide discharging through Δ , 10 k Ω ; \square , 22 k Ω .

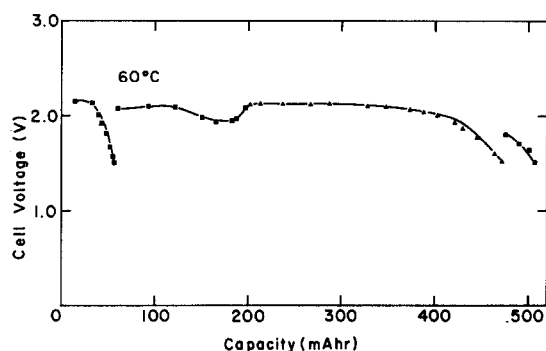


Fig. 4. Discharge curve of an 1130 W h/kg button cell. Solution composition:- 1:3 THF: toluene, 1M LiClO₄ saturated with polysulfide, discharging through 22 k Ω at R.T. and through 10 and 22 k Ω at 60 °C. \blacksquare , 22 k Ω ; \blacktriangle , 10 k Ω .

W h/kg (calculated on the basis of all cell components, excluding the case), at an average voltage of above 2 V. This indicates a self discharge of less than 2.5% per month at 60 °C during continuous discharge.

Button cells of 730 W h/kg discharged at 70 °C through 10 and 22 k Ω loads show a constant voltage above 2. To date the cells have delivered about 40% of their nominal capacity. Cells with the same energy density discharged at -20 °C through 100 k Ω for 2 months exhibit a flat discharge curve of about 2.1 V and have delivered above 70% of their nominal capacity.

The lithium corrosion rates in polysulfide solutions for ampoule tests are shown in Table 1. It can be seen that the corrosion current decreases as the solution becomes rich in toluene. This may be due to the decrease in the solubility of the lithium polysulfide. The capacity loss per month at 60 °C was calculated from the corrosion current, assuming a cell with a capacity of 250 mA h. The capacity loss at 60 °C of Li/S button cells changes from 2 to 5% per month depending on solution composition. This is in fair agreement with the ampoule tests. It may be noticed (Table 2) that Li/SOCl₂ (and

TABLE 1

Lithium corrosion tests at 60 °C
Ampoule tests.

Polysulfide concentration (Molar)	Solvent	Corrosion current ($\mu\text{A}/\text{cm}^2$)	Capacity loss* (% per month)
0.88	THF	14.5	10.4
0.33	THF:toluene 1:1	7.3	5.2
0.1	THF:toluene 1:3	4	2.9

*Calculated for a simulated 250 mA h button cell.

TABLE 2

Capacity loss of Li/SOCl₂ and Li/S cells discharged at 60 °C

Cell type	Capacity (mA h/cm ²)	Discharge current density ($\mu\text{A}/\text{cm}^2$)	Capacity loss (%/month)
Li(SOCl ₂ (C))*	230	40	5
Li/SOCl ₂ (C)*	230	80	10
Li/SOCl ₂ (AA)*	120	60	15
Li/S(Button, 1:3)	220	40 - 80	2.5
Li/S(Button, 1:1)	150	40 - 80	5

*S. Rozen, *Primary High Energy Density Lithium Battery* (A Report, October, 1981).

TABLE 3

Performance of Li batteries — comparison

Cell type	Li/SOCl ₂	Li/MnO ₂	Li/S
Cell voltage (V)	3.66	3.0	2.2
Theoretical energy density (W h/kg)	1500	860	2600
Practical energy density* (W h/kg)	600	400	730(950)**
(W h/l)	820	660	900(1200)**
Practical capacity density* (A h/kg)	164	130	330(430)**
(A h/l)	230	220	400(550)**
Temp. range (°C)	-55 to +70	-20 to +50	-20 to +70
Seal	glass/metal	Organic	Organic
Shelf life (y)	10	4 - 5	10
Cost	high	low	low

*Calculated on the basis of all cell components, excluding the case.

**Discharge at 60 °C.

Li/SO₂ [9]) loses 5 - 15% of capacity per month during discharge at 60 °C depending on initial capacity density and on discharge current density.

Table 3 summarizes the performance of Li/S batteries by comparison with Li/SOCl₂ and Li/MnO₂. The practical energy density is highest in the Li/S cell in spite of the fact that its cell voltage is the lowest. Discharging at 60 °C leads to even better results. The capacity density of Li/S is 2 - 3 times that of the other couples. This means 2 - 3 times greater energy density for all applications for which a voltage lower than 2.2 is sufficient. For instance, CMOS memory backup requires an ideal voltage of 2.0. The temperature range of the cell is -20 to 70 °C. The cell has not yet been checked below -20 °C and above 70 °C. The Li/S, like the Li/MnO₂ cell, can be sealed by an organic elastomer, and so it does not need an expensive glass/metal seal. Corrosion tests at 60 °C clearly indicate a shelf life of at least 10 years.

Acknowledgement

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