

QUANTITATIVE INVESTIGATION OF THE ELEMENTAL SULFUR DISTRIBUTION IN DISCHARGED Li/SOCl₂ CELLS

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Summary

The distribution of elemental sulfur produced during the discharge of Li/SOCl₂ "AA" cells has been studied as a function of electrolyte concentration, temperature, rate and depth of discharge.

Most of the elemental sulfur produced in cells discharged at 5 mA cm⁻² remains within the porous carbon structure of the cathode collector whatever the electrolyte concentration ($0.18 \leq [\text{LiAlCl}_4] \leq 2.36 \text{ mol. dm}^{-3}$) or the temperature (20 °C or 45 °C). In cells containing low electrolyte concentration ($[\text{LiAlCl}_4] \leq 1.35 \text{ M}$) and discharged at 0.34 mA cm⁻², most of the sulfur precipitates on, or close to, the lithium anode. Precipitation of sulfur within the carbon collector can be partially achieved by using a higher electrolyte concentration ($[\text{LiAlCl}_4] \geq 2 \text{ mol. dm}^{-3}$).

1. Introduction

Li/SOCl₂ primary cells have received considerable attention due to their high energy density and wide operating temperature range. In these cells, the liquid SOCl₂ cathode remains in physical contact with the lithium anode. As soon as the lithium and the thionyl chloride come in contact, a spontaneous chemical reaction occurs, resulting in the formation of a passivating, insoluble LiCl film on the anode surface. The low electronic conductivity of this layer gives rise to an insulating, protective film [1] responsible for the potentially long shelf life of these cells.

Li/SOCl₂ cells consist of a lithium anode, an inert, porous carbon electrode and an SOCl₂ solution containing an LiAlCl₄ electrolyte salt. During the electrochemical reduction of SOCl₂ at the porous carbon cathode collector, LiCl, SO₂ and S are produced according to the commonly accepted reaction [2, 3]



Due to this reaction, the cathode collector performances are mainly limited by accumulation of insoluble LiCl within the pore structure of the carbon electrode [4, 5].

Sulfur dioxide is very soluble in the electrolyte through the formation of solvates with Li^+ [6]: elemental sulfur is only sparingly soluble and redistributes inside the cell through a diffusion/convection process. Possible exothermic reaction between the lithium anode and sulfur may occur, especially in discharged cells when the temperature is higher than 150°C [7]. Such temperatures may be reached when the cell is abused, such as by being shorted or forced into overdischarge. Due to their higher specific rate capability, safety hazards such as explosion or violent ventings may occur with spirally-wound type cells.

This paper gives some experimental results dealing with the distribution of elemental sulfur in discharged cells as a function of electrolyte concentration, current density, and depth and temperature of discharge, and thus contributes to a better understanding of safety problems in Li/SOCl₂ cells.

2. Experimental

The conventional Li/SOCl₂ electrolyte consists of a solution of LiAlCl₄ in SOCl₂. This solution is generally prepared by first dissolving the required amount of AlCl₃ in pure SOCl₂ followed by the addition of a stoichiometric amount of LiCl. Four different LiAlCl₄ concentrations were used: 0.18, 0.45, 1.35, and 2.36 mol. dm⁻³. Fluka aluminium chloride and thionyl chloride were used without further purification. Lithium chloride (Fluka) was ground in a mortar and dried under vacuum at 200°C for 24 h. Hydrolysis products were removed from the electrolyte by refluxing.

For these experiments, cylindrical bobbin type cells (AA) were used. Lithium was obtained from Lithcoa: the carbon cathodes were prepared from pure acetylene carbon black and a Teflon emulsion according to a proprietary procedure. The cell case was of stainless steel, the anode contact was nickel and the cell's central pin was made from ferronickel. The cell was hermetically sealed with welded joints and a glass-to-metal seal. The separator material was a non-woven fibreglass from Whatman. Each cell initially contained $3.7 \pm 0.1 \text{ cm}^3$ of electrolyte. Three cells were discharged for given electrolyte concentration and discharge characteristics (temperature, rate and depth of discharge). They were then dismantled for examination using an argon-filled glove box.

2.1. Determination of elemental sulfur

A three step procedure has been used for the determination of elemental sulfur in discharged cells [8].

(i) Vacuum extraction to remove volatile products; SO₂, SOCl₂.

(ii) Carbon disulfide extraction of elemental sulfur by refluxing cell components with CS₂ for 2 h.

(iii) Spectrometric determination of sulfur at 381 nm using a Varian 634 S spectrometer and Suprasil quartz cells (path length 1 cm). The solubility of LiCl and LiAlCl₄ in CS₂ does not interfere in the procedure and can be discounted [8].

After dismantling and vacuum extraction of volatile species, the carbon cathode collectors of the three discharged cells were separated from the other cell components and combined before CS₂ extraction and spectrometric determination of "cathodic sulfur".

The remaining cell components (residual lithium and anode collector, spring and fibreglass separator) were combined and the "anodic sulfur" determination performed using the same procedure.

2.2. Elemental sulfur solubility in SOCl₂-LiAlCl₄ electrolyte

These experiments were carried out using a gravimetric method, and the solubility of sulfur in the above mentioned electrolytes (0.18, 0.45, 1.35 and 2.36 mol. dm⁻³) was determined at 20 and at 45 °C.

3. Results and discussion

3.1. Sulfur solubility

The solubility of sulfur in thionyl chloride as a function of LiAlCl₄ concentration is shown in Fig. 1. As described previously [9] an increase in LiAlCl₄ concentration reduces the sulfur solubility.

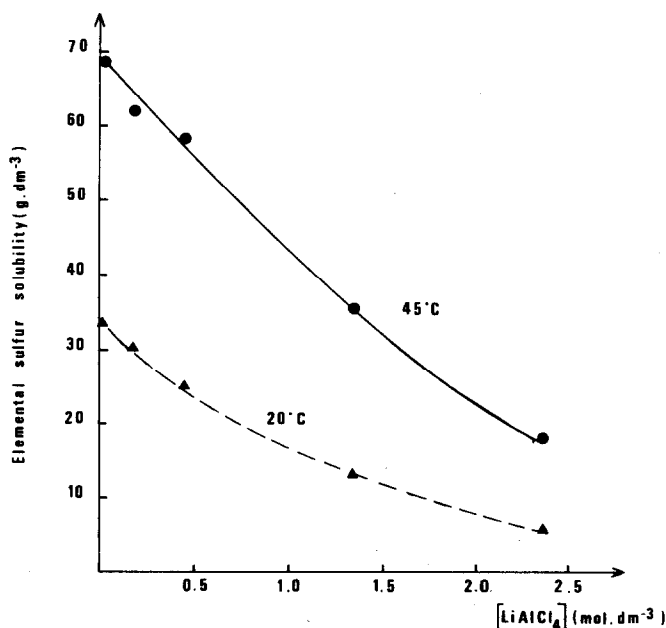
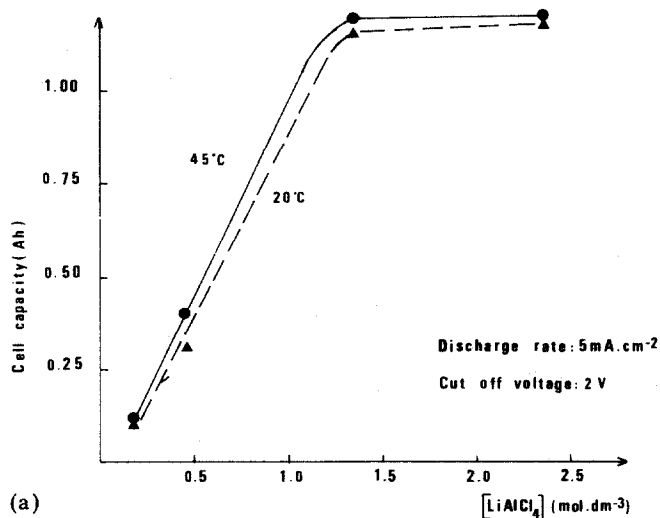


Fig. 1. Elemental sulfur solubility vs. LiAlCl₄ concentration at two different temperatures.

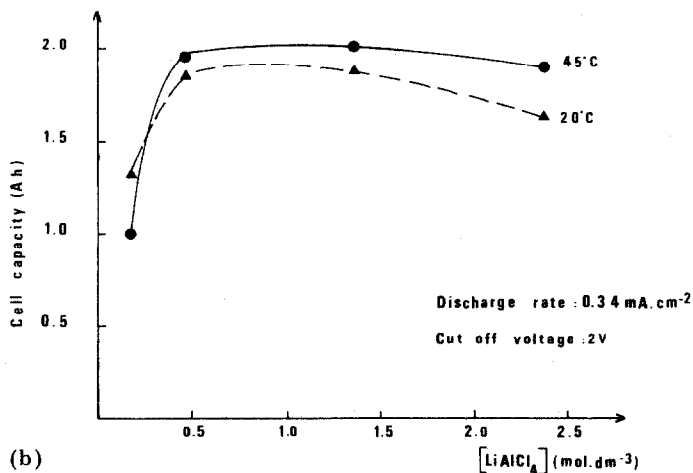
During discharge of Li/SOCl₂ cells, the electrochemical consumption of thionyl chloride increases the electrolyte concentration and consequently reduces the sulfur solubility.

3.2. Discharge capacity

The discharge capacity as a function of electrolyte concentration is given at 20 and at 45 °C for two discharge rates: 5 mA cm⁻² (Fig. 2(a)) and 0.34 mA cm⁻² (Fig. 2(b)) (cut off voltage = 2.0 V).



(a)



(b)

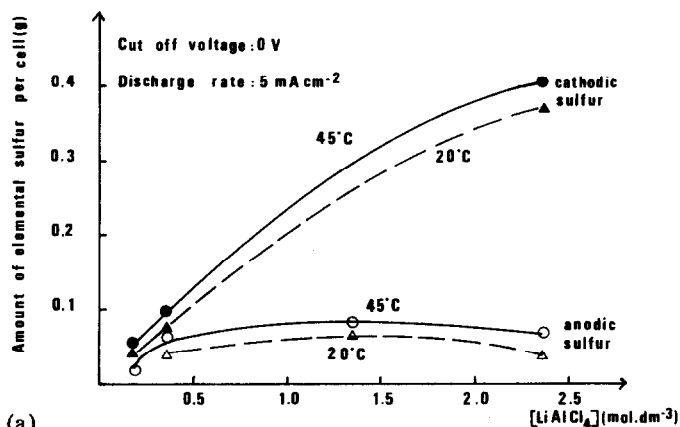
Fig. 2. Discharge capacity of Li/SOCl₂ AA test cells vs. LiAlCl₄ concentration at two different specific discharge rates and temperatures.

3.3. Sulfur distribution

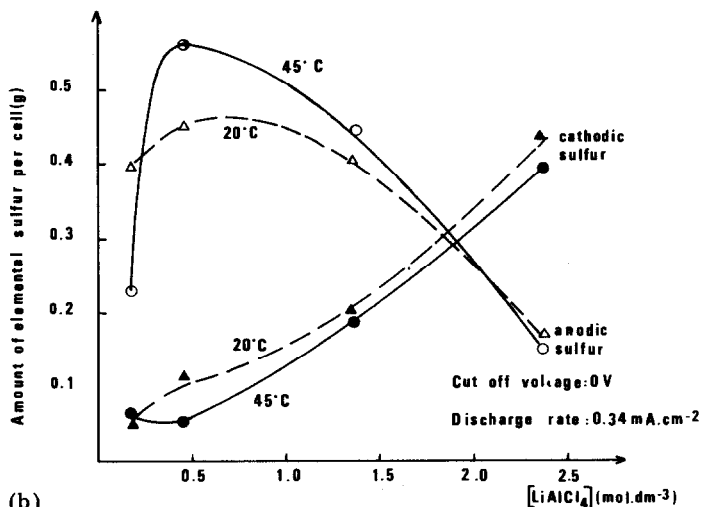
Whatever the discharge conditions, the amount of sulfur recovered in fully discharged cells (cut off voltage = 0 V) agrees with the commonly accepted reaction (1) producing 0.293 g of elemental sulfur per A h.

The distribution of elemental sulfur in 5 mA cm⁻² discharged cells (cut off voltage = 0 V) as a function of electrolyte concentration is shown in Fig. 3(a). For LiAlCl₄ concentrations ranging from 0.18 to 2.36 mol. dm⁻³ the amount of sulfur located within the pore structure of the cathode collector always remains higher than in the anode.

In the case of cells discharged at 0.34 mA cm⁻² (Fig. 3(b)), for [LiAlCl₄] ≤ 1.9 mol. dm⁻³, most of the sulfur is located outside the cathode collector. The amount of anodic sulfur is always higher in low rate than in high rate discharged cells, whatever the electrolyte concentration.



(a)



(b)

Fig. 3. Sulfur distribution within the Li/SOCl₂ AA test cells vs. LiAlCl₄ concentration at two different specific discharge rates and temperatures.

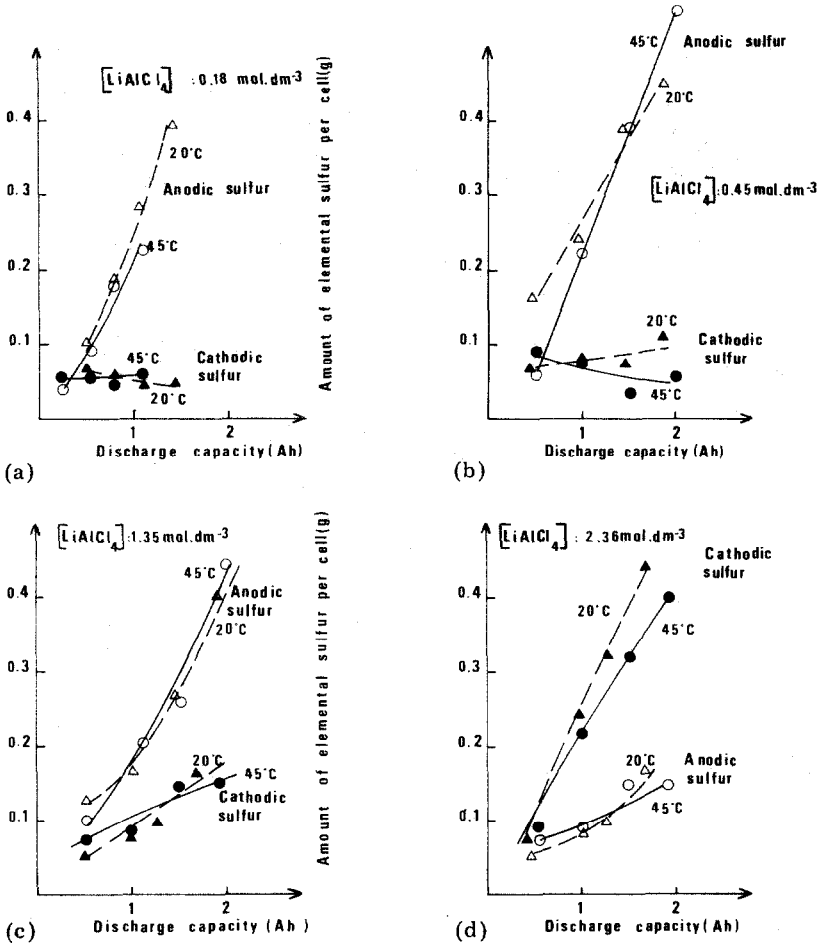


Fig. 4. Sulfur distribution within the Li/SOCl₂ AA test cells vs. discharge capacity for various LiAlCl₄ concentrations and discharge temperatures at a constant specific rate (0.34 mA cm⁻²).

The distribution of sulfur in 0.34 mA cm⁻² discharged cells has been determined at 20 and at 45 °C as a function of depth of discharge. Results obtained for electrolyte concentrations ranging from 0.18 to 2.36 mol. dm⁻³ are shown in Fig. 4.

Whatever the depth of discharge, the distribution of sulfur within the cell depends mainly on the initial electrolyte concentration. Contrary to what is observed for electrolyte concentrations up to 1.35 mol. dm⁻³ (Fig. 4(a) - (c)), the amount of anodic sulfur in cells containing 2.36 mol. dm⁻³ LiAlCl₄ (Fig. 4(d)) is lower than the amount of sulfur located within the cathode collector.

As the discharge proceeds, the electrochemical reduction of thionyl chloride within the pore structure of the carbon electrode gives rise to an

increase in both discharge products and LiAlCl_4 concentrations, resulting in a lowered sulfur solubility.

The local concentration of sulfur within the pores of the carbon cathode depends on both the electrochemical reaction rate (current density) and the diffusion rate of sulfur from the carbon/electrolyte interface to the bulk solution. With high electrolyte concentration and low temperature, diffusion is limited (resulting from higher viscosity) and reduces the rate of mass transport processes. Consequently, the higher the current density and the electrolyte concentration the faster the solubility limit of sulfur will be reached and the higher will be the amount of sulfur precipitated within the cathode.

At low electrolyte concentrations and low rates of discharge, however, diffusional processes dominate and the sulfur distributes throughout the cell. Once its solubility has been exceeded, sulfur precipitates, particularly within the fibreglass separator where it is in close contact with the lithium anode. Moreover, the possible growth of large crystals, such as those observed in some discharged cells, may introduce mechanical stresses, resulting in local internal cell shorts caused by deterioration of the separator. Since an exothermic reaction between lithium and sulfur may occur when cells are abused, such sulfur precipitation on or close to the lithium must be avoided. The latter may perhaps explain some unexpected violent chemical reactions which have been observed, in some cases with cells partially discharged during storage.

Conclusion

The elemental sulfur distribution in discharged Li/SOCl_2 bobbin type 'AA' cells has been quantitatively determined as a function of:
electrolyte concentrations of 0.18, 0.45, 1.35 and $2.36 \text{ mol. dm}^{-3}$;
temperatures of 20 and $45 \text{ }^\circ\text{C}$;
rates of discharge of 5 mA cm^{-2} and 0.34 mA cm^{-2} ;
depth of discharge.

Most of the elemental sulfur produced in cells discharged at 5 mA cm^{-2} precipitates within the porous carbon structure, whatever the electrolyte concentration and temperature. In cells discharged at a low rate, and when the electrolyte concentration is lower than 1.5 mol. dm^{-3} , most of the sulfur precipitates outside the cathode, within the fibreglass separator and on the internal metallic components of the cell. The sulfur distribution within the cell depends mainly on the initial electrolyte concentration, whatever the depth of discharge.

Acknowledgements

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