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Journal of Power Sources 55 (1995) 107–109

JOURNAL OF POWER SOURCES

Short Communication

Study of sealing quality of small $Li/SOCl_2$ cells

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Received 14 September 1994; accepted 10 November 1994

Abstract

An examination is made of the sealing of small $Li/SOCl_2$ cells in a high-temperature condition (200 °C). The metal/metal weld has good quality, but the glass/metal connection between the terminal pin, insulator and the lid is relatively poor. The development of cracks in the insulator, that originate from the Griffith microseam, is due to the combined reaction of temperature, pressure, stress corrosion and bubbles.

Keywords: Sealing; Lithium/thionyl chloride cell; Cell failure

1. Introduction

The shelf life of a cell is strongly affected by the sealing quality. Recently, there have been many advances in this property for Zn/Mn and Pb/acid cells. These have resulted in a marked improvement and development in the shelf life and working life of such cells [1–5]. For an $Li/SOCl_2$ cell, as the electrolyte ($SOCl_2$) is extremely corrosive, a hermetic seal has been used widely in both laboratory research and industrial production [6]. Nevertheless, there is a continuous need to solve the sealing problem and to perfect the technique. Otherwise, considerable effort must be made to produce miniature cells that have small dimensions and complex technology. Some manual operations are also involved in the cell fabrication.

The failure of $Li/SOCl_2$ cells at room temperature is largely accompanied by leakage of electrolyte. Consequently, a thick layer of corroded material is formed on the outside of the cell can. In the work reported here, a heating method is used to accelerate the failure process. At the same time, a variety of cell-sealing conditions are monitored. The aim of the research is to obtain useful information on the improvement of the sealing process.

2. Experimental

All the test cells were newly manufactured with the same technology. The cell dimensions were: diameter 11.5 cm and height 15 mm. The stainless-steel can was hermetically sealed and the glass/metal seal was made from a ceramic-like material.

The cells were placed in an oven maintained at a temperature of 200 °C. An examination of the leakage and failure processes was made at regular intervals.

The characteristics of the connection and sealing conditions were investigated by use of a scanning electron microscope.

3. Results and discussion

Research into sealing methods is a basic requirement for the production of cells with a long shelf life. Secure sealing can prevent not only leakage of electrolyte but also the ingress of vapour and oxygen. Inside the cell, both the stainless-steel and the glass/metal seal are in direct contact with $SOCl_2$. In order to achieve high corrosion-resistance, careful selection of the stainless-steel components and good thermal treatment of the steel are essential [7] because of the aggressive nature of the electrolyte. No leakage phenomenon was found in the connection between the lid and the cell can in all of the tested cells. This was due to application of the SIG technique for the metal-to-metal connection. The method is widely used in the battery industry. By contrast, leakage with observed in the connection region of the ceramic and the positive terminal pin. This connection was perfect in only a few of the cells. Bubbles were detected in the glass/metal seal (Fig. 1)

SSDI 0378-7753(94)02167-2

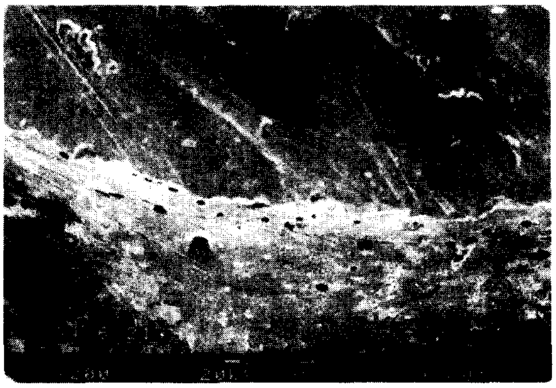

Fig. 1. Electron micrograph showing bubbles in ceramic seal insulator; magnification ×200.

Fig. 2. Electron micrograph of connection between pin and ceramic seal insulator; magnification ×120.

Table 1
Degradation of small $Li/SOCl_2$ cells at 200 °C

Cell	Number of cells	Type of degradation	
		Explosion	Deformation
A-92	6		6
A-293-O	5	2	3
A-93-N	5	1	4
A-94	15	5	10
Total	31	8	23

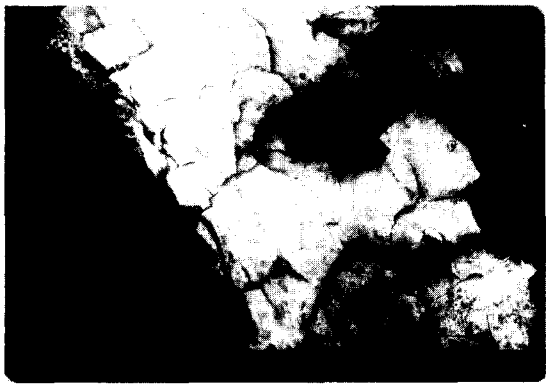

Fig. 3. Electron micrograph showing cracks in ceramic around terminal pin; magnification ×100.

and were formed when the ceramic seal was multi-welded. These bubbles encourage the development of cracks at high temperature. Thirty-one cells, in four groups, were treated at 200 °C in the oven for different periods. The results are given in Table 1.

At high temperature, the main reason for the rise in internal pressure is a decrease in the dissolution of SO_2 in the electrolyte [8,9]. Acceleration of the self-discharge reaction and a build-up of the vapour pressure can both cause the internal pressure to increase. At a certain internal pressure, most of the cells exhibited bulges in the bottom section and cracks in the ceramic seal. The latter was the major cause of cell failure. In some of the other cells, however, the seal enjoyed a tighter bond (Fig. 2) with the stainless steel. In other words, the connection had higher strength, and as the pressure intensity is greater than the strength of stainless steel, the can could explode.

The internal pressure (about 6 MPa [10]) of a deformed cell can be calculated from the elasticity [11]. Assuming that the raised cell bottom approximates to that of a sphere, the following formula can be used to calculate the pressure intensity in an exploded cell:

$$\sigma_T = \frac{1/(2R^a) + 1/b^a}{1/a^a - 1/b^a}\, q \tag{1}$$

where σ_T is the stress on the internal bottom, a the internal radius of the sphere, b the outside radius of the sphere, q the internal pressure, and R the average radius of the sphere. When the thickness of the cell can is 0.37 mm, and $R = a = 20$ mm, $b = 20.37$ mm, $\sigma_T = \sigma_b = 390$ MN m^{-2} [12], Eq. (1) yields:

$$q = \frac{\sigma_T}{28.76} = \frac{\sigma_b}{28.76} = \frac{490}{28.76} = 17 \text{ MN m}^{-2} = 17 \text{ MPa} \tag{2}$$

The value (17 MPa) is actually the pressure-resistant strength of the ceramic seal insulator.

The condition of the joint between the ceramic seal insulator and the stainless-steel terminal pin can be seen in the electron micrograph presented in Fig. 3. It is concluded that both separation of the ceramic and stainless steel, and numerous cracks in ceramic itself, caused the cell to fail. The connection of glass/metal seal is different to that of the metal/metal seal. A tight bond can be achieved between two kinds of suitable metals, as mentioned above for the stainless steel/stainless steel couple. A ceramic material, however, cannot melt with a metal to form a uniform seal. Therefore, it will be easily separated from the metal, and the electrolyte will leak through the resulting cracks. According to the Griffith theory of the strength of glass/

ceramics, microseams develop in brittle materials as a result of the presence of lattice defects. A brittle break may occur when these microseams are affected by a stress that is far less than the breaking strength of the steel σ_T. The latter is given by:

$$\sigma_T = \sqrt{\frac{2Er}{(1-\mu^2)\pi C}} \tag{3}$$

where C is the half-length of the microseams, μ the Poisson ratio, r the breaking energy per unit surface area, and E the modulus of elasticity.

It is clear that breakage of the ceramic seal insulator is attributed to the internal stress. For small $Li/SOCl_2$ cells, there is also the influence of stress corrosion and thermal stress. These both served to decrease further the sealing stability. Heating at 200 °C causes an acceleration of the various chemical and electrochemical processes that take place within the cell. Thus, the results given here might not agree with those obtained during room temperature storage. Under the latter conditions, the major factors are that the observation takes a very long period, and that the phenomenon is not distinct.

4. Conclusions

Under the accelerating condition of 200 °C, the sealing quality of some kinds of small $Li/SOCl_2$ cells was examined and analysed. With the present level of sealing technology, the welding between the metal/metal can provides good sealing properties, but the metal/ceramic junction is vulnerable. Temperature, pressure and stress corrosion can all cause cracking of the ceramic seal insulator. This gives rise to the escape of $SOCl_2$ vapour and, finally, to cell failure. The quality of the ceramic material is a strong determinant of the sealing quality.

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