

# *The i.r. analysis of water traces in electrolytes for Li/SOCl<sub>2</sub> cells*

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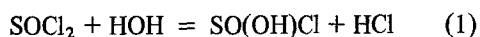
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It is established that the absorbance of the SOCl<sub>2</sub>/LiAlCl<sub>4</sub> electrolyte solutions at 2800 cm<sup>-1</sup> is due the HCl, generated in the solution as a result of the hydrolysis reaction of SOCl<sub>2</sub>. A slow 'self-desiccation' reaction of the hydrated Al(OH)Cl<sub>2</sub> is also postulated to occur in these solutions.

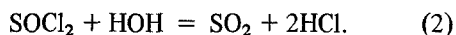
## 1. Introduction

The water content in thionyl chloride electrolytes used for Li cells is usually kept below 10-20 ppm [1, 2]. The determination of water in this highly oxidizing solution is, as yet, only possible by i.r. spectroscopy. The method developed by French *et al.* [3] has already found practical application [1]. The basic results of these authors [3] could be summarized as follows:

(a) In the presence of water in pure SOCl<sub>2</sub> the i.r. spectrum has an absorption band at 2800 cm<sup>-1</sup>, assigned to SO(OH)Cl formed according to the reaction



which differs from the generally accepted hydrolysis reaction



(b) After the addition of AlCl<sub>3</sub> to SOCl<sub>2</sub> the peak at 2800 cm<sup>-1</sup> completely disappears as a result of the reaction:



and a new peak at 3380 cm<sup>-1</sup>, due to Al(OH)Cl<sub>2</sub>, appears.

Our own experience with the application of the method of French *et al.* [3] has led to some

new facts which should be kept in mind when this method is applied for quantitative analysis.

## 2. Experimental

All reagents were AR grade (Merck). AlCl<sub>3</sub> was additionally purified by triple sublimation. LiCl was dried in a vacuum by a gradual temperature increase up to 380° C. The electrolyte preparation was carried out in a Perspex glove dry box flushed with argon. The water content in the box was maintained below 20 ppm. The i.r. spectra were recorded on a UR-20 Carl-Zeiss-Jena i.r.-spectrophotometer in 0.5 cm quartz cells. Prior to each measurement the cells were kept in the dry box for one day in order to remove adsorbed moisture.

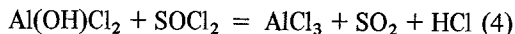
## 3. Results and discussion

The spectrum of a freshly prepared 1 M LiAlCl<sub>4</sub> solution in SOCl<sub>2</sub> (Fig. 1a) shows two absorption peaks at 2800 and 3400 cm<sup>-1</sup> in agreement with [3]. It was established that although the peak at 2800 cm<sup>-1</sup> diminishes with time it did not disappear completely even after 6 months storage in a closed vessel placed in the dry box.

Passing dry argon through this solution for 3-4 min led, however, to the complete disappear-

ance of the  $2800\text{ cm}^{-1}$  peak (Fig. 1b), while the absorption band at  $3400\text{ cm}^{-1}$  remained almost unchanged. This finding suggests that the absorption at  $2800\text{ cm}^{-1}$  is due to some volatile component in the solution, presumably HCl. In order to verify this assumption, dry gaseous HCl was passed through the electrolyte and this resulted in the appearance of a strong band at  $2800\text{ cm}^{-1}$  (Fig. 1d). Data on the absorption of HCl in various solvents at about  $2800\text{ cm}^{-1}$  are reported in [4, 5].

A series of experiments were carried out to assess the stability of the hydrolysis products with time. Table 1 presents the decrease of the absorbance ( $A$ ) at  $2800$  and  $3400\text{ cm}^{-1}$  during 11 days. It can be seen that the concentrations of both hydrolysis products diminish with time. A 'self-desiccation' reaction



might be postulated.

The HCl generated according to Reaction 4 in the solution is gradually lost, as shown by the results in Table 1.

In another experiment a  $1\text{ M LiAlCl}_4$  solution was flushed with argon (Fig. 1e) so that the peak

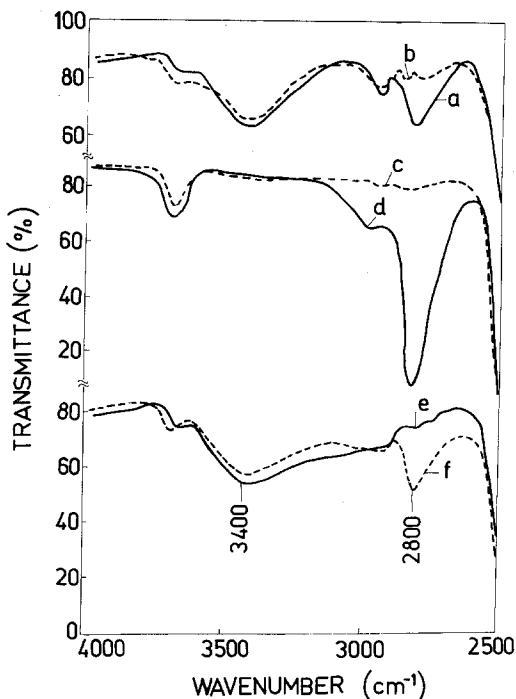


Fig. 1. i.r. spectra: (a) freshly prepared  $1\text{ M LiAlCl}_4$  in  $\text{SOCl}_2$ ; (b) the same after 3 min bubbling with dry Ar; (c)  $\text{SOCl}_2$  after 3 min bubbling with dry Ar; (d) the same after 3 min bubbling with dry HCl (gas); (e)  $1\text{ M LiAlCl}_4$  in  $\text{SOCl}_2$  after 3 min bubbling with dry Ar; (f) the same after 24 hours storage.

Table 1. Variation with time of absorbances at  $2800$  and  $3400\text{ cm}^{-1}$  for  $\text{LiAlCl}_4(1\text{ M})$  in  $\text{SOCl}_2$

| Days | $A_{3400}$ | $A_{2800}$ |
|------|------------|------------|
| 0    | 0.300      | 0.204      |
| 7    | 0.163      | 0.163      |
| 11   | 0.135      | 0.154      |

at  $2800\text{ cm}^{-1}$  was totally removed. It was left for 24 hours and then re-analysed. The reappearance of the HCl peak (Fig. 1f) and the slight decrease of the  $3400\text{ cm}^{-1}$  peak is in agreement with the 'self-desiccation' reaction (Reaction 4). Unfortunately the  $\text{SO}_2$  absorption cannot be observed in quartz cells.

The above findings lead naturally to the following conclusions regarding the application of the method of French *et al.* [3]:

(a) It seems to be incorrect to analyse water in pure  $\text{SOCl}_2$  using the peak at  $2800\text{ cm}^{-1}$ . The latter, due to HCl, will be proportional to the concentration of water in  $\text{SOCl}_2$  only if precautions are taken to prevent the escape of HCl from the solution.

(b) The construction of a calibration curve at  $3400\text{ cm}^{-1}$  for the determination of water in  $\text{SOCl}_2$  electrolytes by the addition of known amounts of  $\text{H}_2\text{O}$  is also unreliable since a considerable fraction of the water reacts with  $\text{SOCl}_2$  according to Reaction 2.

(c) A more correct approach in the construction of a calibration curve would be to add  $\text{AlCl}_3$  with a known  $\text{H}_2\text{O}$  content to the  $\text{SOCl}_2$ . The possibility of 'self-desiccation' still cannot be neglected.

From the practical point of view it is important to note that i.r. spectra give data for the concentration of HCl. The latter, due to its depassivation effect [6], might deteriorate the performance of the Li/ $\text{SOCl}_2$  cell.

## References

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