

***In situ* Raman spectra of the discharge products of calcium and lithium-anoded thionyl chloride cells — sulphur dioxide generation in oxyhalide systems**

W. P. Hagan* and **D. G. Sargeant**

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU (U K)

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Abstract

A cell has been constructed that allows a calcium or lithium-anoded oxyhalide cell of conventional composition to be analysed for catholyte-soluble discharge products using laser Raman spectroscopy. Both cells showed the presence of sulphur dioxide solvated by thionyl chloride. Species of the type $M(\text{SOCl}_2)(\text{SO}_2)_n^{+}(\text{AlCl}_4)_n^{-}$ could only be detected in cells having calcium or lithium anodes with LiAlCl_4 as the supporting electrolyte in thionyl chloride. Vapour pressure measurements of discharging cells confirmed that $\text{Ca}(\text{AlCl}_4)_2$ was less likely to form a complex with sulphur dioxide than the analogous lithium salt.

Introduction

The ultimate fate of sulphur dioxide produced from the reduction of thionyl chloride and sulphuryl chloride has received little attention until quite recently. Although sulphur dioxide produced as a consequence of the reduction of the oxyhalides is not responsible for cathode failure, it is partially soluble in the electrolyte solution [1]. However, the vapour pressure of a sulphur dioxide-containing electrolyte solution, particularly at, or near, saturation, will be considerably higher than that in the absence of sulphur dioxide.

Two significant consequences of the presence of solvated sulphur dioxide, and the vapour pressure it could exert in a sealed cell, particularly towards the end of discharge are: (a) reduced safety margins, (b) the necessity for safety venting in even quite small cells. Recent reports in the literature [2] have suggested that sulphur dioxide produced in lithium/thionyl chloride cells can form a stable complex with the lithium tetrachloroaluminate supporting electrolyte to form $(\text{Li}(\text{SOCl}_2)(\text{SO}_2)_n)^{+}(\text{AlCl}_4)^{-}$.

In this communication we present our results from a Raman spectroscopic examination of the discharge products of lithium and calcium-based cells with thionyl chloride catholytes, lithium and calcium tetrachloroaluminate supporting electrolytes, and porous-carbon current collectors.

*Author to whom correspondence should be addressed. Present address: Department of Chemistry, Leicester Polytechnic, P O Box 143, Leicester LE1 9BH, U K

Experimental

Lithium metal foil (99.9+%Li, Battery quality) was obtained from the Lithium Corporation of America (LITHCO) Calcium metal originated from Pfizer Inc and was rolled to a final thickness of 250 μm by PFM Alloys After mechanical abrasion of the oxide coating, the metal foil was degreased in dried, distilled acetone, and dried Both metals and all materials were preformed in dry boxes, <0.1% relative humidity at 20 °C

Electrolyte solutions were prepared by dissolving the required amounts of AlCl_3 in redistilled SOCl_2 , the appropriate molar equivalent of either anhydrous LiCl , NaCl , CaCl_2 , or SrCl_2 was then added and refluxed for 4 h to ensure complete solubilisation

Purum grade SOCl_2 originated from Fluka, as did the anhydrous AlCl_3 and LiCl which were dried at 300 °C in a vacuum oven before being transferred to a dry box Anhydrous SrCl_2 and CaCl_2 were obtained from Ventron (Alfa Products) and Fluka, respectively these were used as received The NaCl from B D H (AnalaR) was vacuum dried at 300 °C

Sulphur dioxide complexes of the tetrachloroaluminate salts were prepared by passing SO_2 over a mixture of anhydrous AlCl_3 and the chosen anhydrous metal halide (LiCl , CaCl_2 , or SrCl_2) The coordination number of SO_2 was determined by evaporating a known weight of complex to constant weight thereby removing all complexed SO_2 Raman spectra of the solid remaining after evaporation confirmed the absence of complexed or adsorbed SO_2 in the sample

Sulphur dioxide saturated solutions of LiAlCl_4 , $\text{Ca}(\text{AlCl}_4)_2$, and $\text{Sr}(\text{AlCl}_4)_2$ in SOCl_2 and SO_2Cl_2 were prepared by adding an excess of SO_2 and allowing

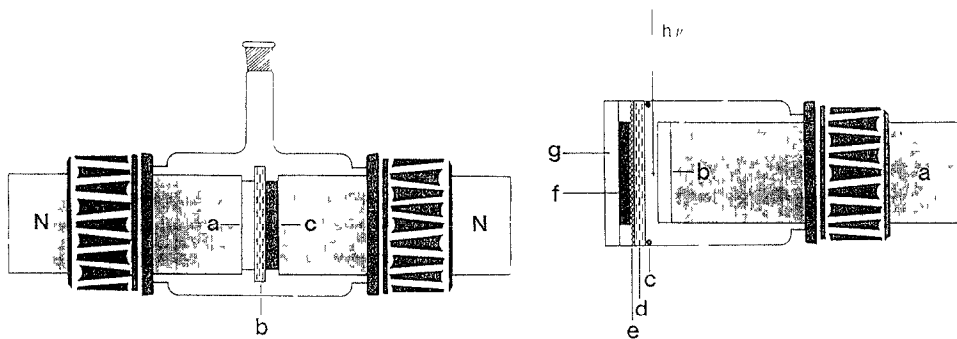


Fig 1 Cell for vapour pressure measurement of electrolyte solutions during discharge N, N', nickel plungers retained by screw thread caps into the pyrex body and sealed by 'Viton' 'O' rings The cell components comprising a, anode, b, ceramic separator, c, carbon current collector, were compressed between the nickel plungers that acted as electrical feed-throughs

Fig 2 Cell for measurement of *in situ* laser Raman spectra of electrolyte solutions during discharge The cell comprised a, nickel plunger retained by a screw thread cap and sealed with a 'Viton' 'O' ring, b, lithium or calcium anode, c, circlip retainer, d, separator paper, e, nickel mesh, f, carbon current collector, g, vitreous carbon end-cap acting as an electrical feed through to the carbon current collector

the resultant solutions to reach their equilibrium saturation concentrations over a period of 2 h at room temperature

Vapour pressures and discharge curves of lithium and calcium-anoded SOCl_2 cells were measured in the cell shown in Fig. 1. It consisted of a lithium or calcium anode, Shawinigan Acetylene Black (SAB) cathode, and a ceramic paper separator. The modified outer casing permitted vapour pressure measurement by a modified isothermometric method. The whole assembly was maintained in a water bath to within $\pm 0.1^\circ\text{C}$ of any required temperature.

The laser Raman spectra of catholyte solutions at various stages of discharge were measured using a cell similar to that depicted in Fig. 2. Cells were discharged at 21°C ($\pm 2^\circ\text{C}$) in the sample compartment of the Raman spectrometer. A double monochromator was used to record the Raman spectra of the catholyte solutions. A slightly larger ($\sim 1\text{ mm}$) than usual interelectrode separation was required to facilitate electrolyte sampling by the laser beam. The excitation line used for the scattering experiments was at 488 nm (argon ion laser) and typically had a power of 20 mW at the sample position. As glass is a weak Raman scatterer the cell design was greatly simplified. Cells were discharged galvanostatically.

Results and discussion

Raman spectra, reproduced in Figs 3 and 4, are for SO_2 saturated solutions of LiAlCl_4 , $\text{Ca}(\text{AlCl}_4)_2$, and $\text{Sr}(\text{AlCl}_4)_2$ in thionyl chloride and sulphuryl chloride, respectively. Bands at 1230 cm^{-1} and shoulders at 1202 cm^{-1} in Fig. 3 have been assigned to free SOCl_2 and SOCl_2 molecules bonded to either Li^+ or Ca^{2+} [2] and are associated with a stretching mode of the S-O bond. In the case of the lithium-based tetrachloroaluminate salt, two peaks are resolved with maxima at 1144 cm^{-1} and 1160 cm^{-1} . The formation of an $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+(\text{AlCl}_4)^-$ complex has been characterised by a band appearing at 1160 cm^{-1} [2]. This band is associated with a vibrational mode of SO_2 molecules bonded to the Li^+ cation. The 1144 cm^{-1} band corresponds to 'free' SO_2 molecules. In this sense 'free' still requires SO_2 molecules to be solvated by either thionyl or sulphuryl chloride, but there is no definite bond to the Li^+ cation. A similar situation exists in SO_2 saturated solutions of the calcium-based tetrachloroaluminate salt, with the major difference being a much reduced intensity of the 1160 cm^{-1} band relative to the 1230 cm^{-1} band. The 1160 cm^{-1} band is absent in the strontium tetrachloroaluminate solution in both thionyl and sulphuryl chlorides. For both the lithium and calcium-based salts the band intensity at 1160 cm^{-1} is enhanced in sulphuryl chloride, which may be attributed to the change in geometry of the solvent molecule. Previously published Raman studies [3, 4] of $\text{Ca}(\text{AlCl}_4)_2$ in SO_2Cl_2 with added SO_2 have also identified bands at 1145 cm^{-1} , and the higher energy band at 1155 cm^{-1} , also believed to be due to SO_2 molecules complexing with calcium cations.

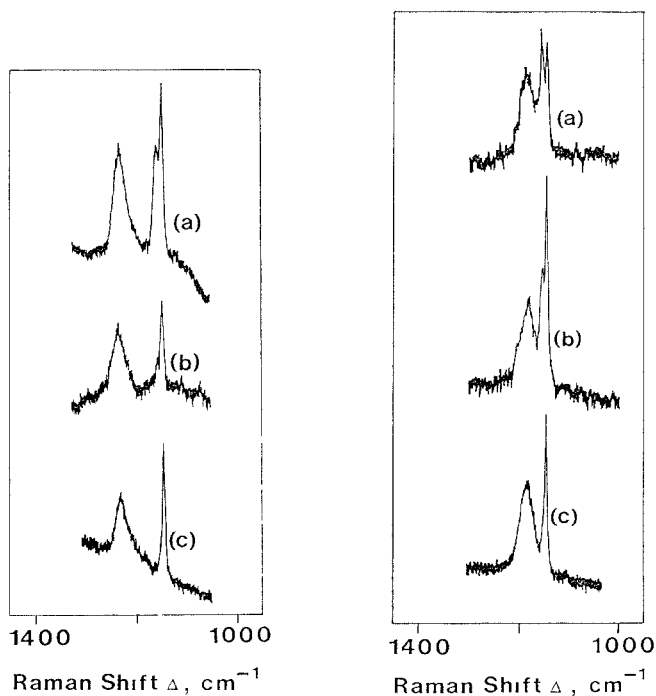


Fig 3 Raman spectra of SO_2 saturated solutions of (a) 1.8 M LiAlCl_4 , (b) 1.5 M $\text{Ca}(\text{AlCl}_4)_2$, (c) 1.0 M $\text{Sr}(\text{AlCl}_4)_2$ in thionyl chloride

Fig 4 Raman spectra of SO_2 saturated solutions of (a) LiAlCl_4 , (b) 1.5 M $\text{Ca}(\text{AlCl}_4)_2$, (c) 1.0 M $\text{Sr}(\text{AlCl}_4)_2$ in sulphuryl chloride

It appears that while a complex of the type $\text{Li}(\text{SO}_2)_n^+(\text{AlCl}_4)^-$ is readily formed in thionyl and sulphuryl chlorides, the analogous calcium complex is less favoured in both solvents, and is not formed at all with the strontium compound

For comparison, Raman spectra of pure, liquid $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$, $\text{Ca}(\text{SO}_2)_3(\text{AlCl}_4)_2$, and $\text{Sr}(\text{SO}_2)_2(\text{AlCl}_4)_2$ are shown in Fig 5. The lithium compound has bands at 1160 cm^{-1} and 1170 cm^{-1} and the calcium compound at 1144 cm^{-1} and 1160 cm^{-1} , while the strontium compound has a single, broad band at 1155 cm^{-1} . The higher energy band has been assigned in the case of lithium to SO_2 molecules bonded to Li^+ in a manner similar to that of a chain-like arrangement observed in the solid phase. The 1330 cm^{-1} band common to all three spectra is associated with an asymmetric stretch of the S-O bond in sulphur dioxide [2].

Figure 6 shows *in situ* Raman spectra of a calcium-anoded cell with a 1.0 M $\text{Ca}(\text{AlCl}_4)_2$ solution in thionyl chloride. In addition to the increasing resolution of the solvent peaks with discharge, a peak can be identified at 1144 cm^{-1} in the 50% and 100% discharged cell. In this and subsequent examples, 100% discharge is taken to mean the discharge time to 0 V. In

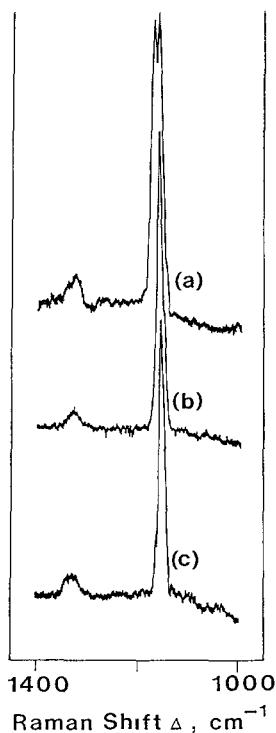


Fig 5 Raman spectra of (a) pure $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$, (b) pure $\text{Ca}(\text{SO}_2)_3(\text{AlCl}_4)_2$, (c) pure $\text{Sr}(\text{SO}_2)_2(\text{AlCl}_4)_2$

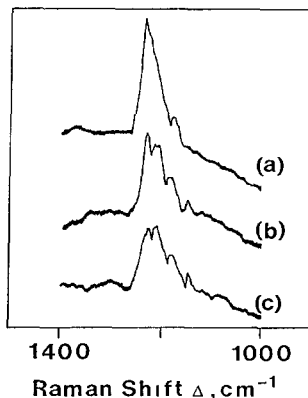


Fig 6 *In situ* Raman spectra of 1.5 M $\text{Ca}(\text{AlCl}_4)_2$ electrolyte solution in a calcium-anoded cell at (a) open circuit before discharge, (b) 50% discharge, (c) 100% discharge (0 V). The cell was discharged at the 10 mA cm^{-2} rate at $21 \pm 2 \text{ }^\circ\text{C}$

contrast to Fig. 3, this peak at 1144 cm^{-1} is attributed to free SO_2 produced as a consequence of the reduction of thionyl chloride. The absence of a peak at 1160 cm^{-1} is an indication that a complex of the type $\text{Ca}(\text{SOCl}_2)(\text{SO}_2)^{2+}(\text{AlCl}_4)_2^-$ does not form readily or in appreciable concentration.

Figure 7 illustrates the results of a similar experiment using a calcium-anoded cell but with 1.8 M LiAlCl_4 solution in thionyl chloride as the catholyte. At 50% and 100% discharge, two peaks, at 1144 cm^{-1} and 1160 cm^{-1} , appeared, suggesting that both free SO_2 , and complexed SO_2 in the form $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+(\text{AlCl}_4)^-$, are present in the solution. We have already suggested that calcium tetrachloroaluminate complexes with SO_2 may not be formed as readily as the lithium complex in thionyl chloride, and these results confirm that this situation persists in a discharging cell. For comparison, the spectra of a lithium-anoded cell with a 1.8 M LiAlCl_4 solution in thionyl chloride are shown in Fig. 8. On discharge, peaks appear at 1144 cm^{-1} and 1160 cm^{-1} , suggesting the presence of free and complexed SO_2 . An earlier

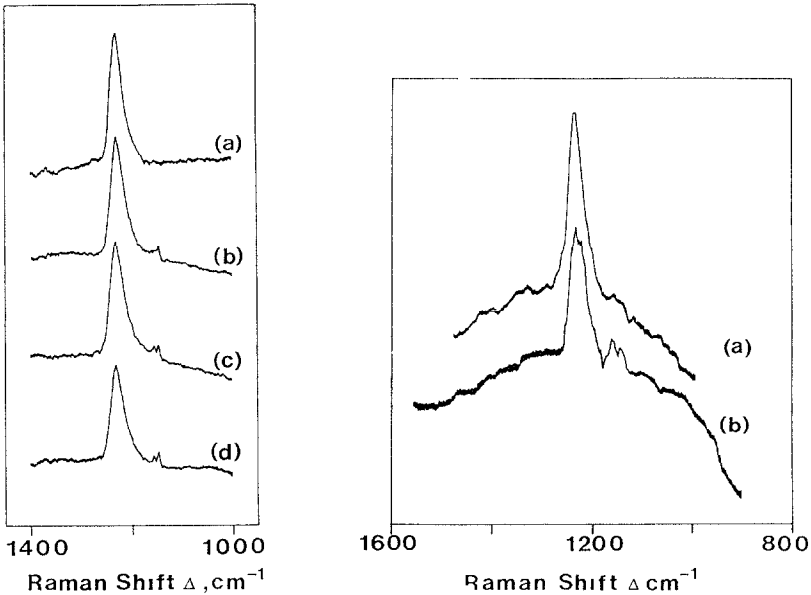


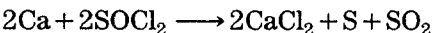
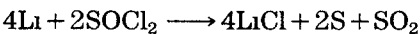
Fig 7 *In situ* Raman spectra of a 1.8 M LiAlCl_4 electrolyte solution in a calcium-anoded cell at (a) open circuit before discharge, (b) 25% discharge, (c) 50% discharge, (d) 100% discharge (0 V). The cell was discharged at the 10 mA cm^{-2} rate at $21 \pm 2^\circ \text{C}$.

Fig 8 *In situ* Raman spectra of a 1.8 M LiAlCl_4 electrolyte solution in a lithium-anoded cell at (a) open circuit before discharge, (b) 50% discharge. The cell was discharged at the 50 mA cm^{-2} rate at $21 \pm 2^\circ \text{C}$.

worker [2] had only detected the presence of complexed SO_2 , but this may be due to differences in cell design and to the fact that the present cell incorporates a porous carbon cathode rather than the graphite employed in the cell described in the literature. A graphite cathode will be readily covered with solid state reaction product and the shorter discharge times will produce much less SO_2 than for a porous carbon cathode.

The fact that there are such clear differences in the abilities of calcium and lithium-based catholytes to complex SO_2 should be reflected in the internal cell pressures produced during discharge. In practical terms this may mean that certain cell compositions require provision for venting excess pressure if high rate discharges are required. A major US manufacturer of lithium/thionyl chloride cells recognises that there is no need to provide an excess pressure vent for low rate applications in cells up to AA size [5].

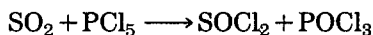
Comparison of overall cell reactions for lithium and calcium thionyl chloride cells



reveals that, per mole of metal, twice as much SO_2 is produced in calcium-anoded systems. As we have already shown, calcium's ability to complex

SO₂ is limited when compared with lithium tetrachloroaluminate. A situation could exist where the inherent safety of a calcium-based system was compromised by internal pressure build-up

Early work on lithium/thionyl chloride systems concluded, from pressure measurements at room temperature, that there was no major product build-up in the gas phase. The data indicated that battery use would not be restricted by pressure generation, either during storage or on discharge [6]. A recent U S Patent [7] describes the use of PCl₅ to scavenge SO₂ produced as a consequence of high-rate discharge of lithium/thionyl chloride batteries.



Such procedures might have more relevance to calcium/thionyl chloride cells if uncomplexed SO₂ were available to contribute to the internal pressure.

Simultaneous recording of vapour pressure/cell voltage curves for discharging cells allows the contribution of SO₂ to the vapour pressure, at various states of discharge, to be estimated. Once it has been established that the vapour pressure of complexed SO₂, as Li(SO₂)₃AlCl₄, is not very different from the catholyte solution, complexation during discharge should keep internal pressures within acceptable limits. The vapour pressures, at 25 °C, of Li(SO₂)₃(AlCl₄) and Ca(SO₂)₃(AlCl₄)₂, shown in Table 1, are 0.123 bar and 0.244 bar, respectively, while the vapour pressures of the uncomplexed tetrachloroaluminate solutions in thionyl chloride at 25 °C are 0.125 bar (1.8 M LiAlCl₄) and 0.122 bar (1.5 M Ca(AlCl₄)₂).

Figure 9 shows a cell potential/vapour pressure curve for a lithium/thionyl chloride system at 25 °C discharged at 50 mA cm⁻². The curve shows a pressure increase of about 6% as the cell voltage falls to 90% of the average plateau voltage (0.9 *E*_{avg}). This should be compared with Fig. 10, which is for a calcium/thionyl chloride cell showing a 16% increase in vapour pressure. There is only an 11% increase in vapour pressure when 1.0 M LiAlCl₄ is used as the supporting electrolyte. Table 2 also shows vapour pressure data for calcium anoded-cells with strontium and sodium tetrachloroaluminate supporting electrolytes.

We consider that in thionyl chloride solutions the major factor affecting the ability of SO₂ to complex with the cation is the strength of the interaction

TABLE 1

Vapour pressures of pure liquids and solutions at 25 °C

Compound	Vapour pressure at 25 °C (bar)
SOCl ₂	0.147
SOCl ₂ + 1.8 M LiAlCl ₄	0.125
SOCl ₂ + 1.5 M Ca(AlCl ₄) ₂	0.122
Li(SO ₂) ₃ AlCl ₄	0.123
Ca(SO ₂) ₃ (AlCl ₄) ₂	0.244
Sr(SO ₂) ₂ (AlCl ₄) ₂	0.396

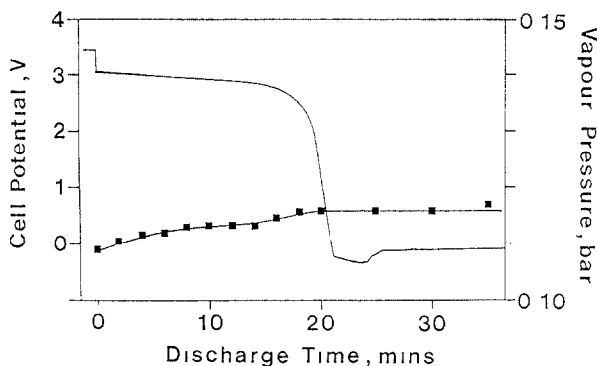


Fig 9 Cell potential/vapour pressure for 1.8 M LiAlCl_4 in thionyl chloride with a lithium anode and SAB cathode discharged at 50 mA cm^{-2} at 25°C . Vapour pressure datum points (■) pertain to the right-hand vapour pressure ordinate.

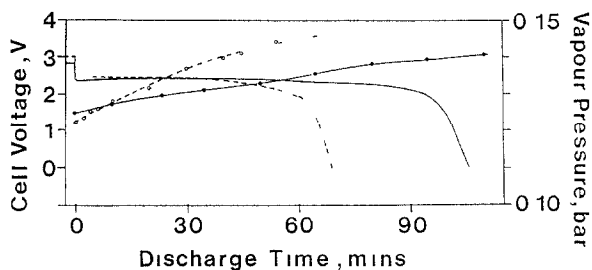


Fig 10 Cell potential/vapour pressure for 1.0 M $\text{Ca}(\text{AlCl}_4)_2$ in thionyl chloride with a calcium anode and SAB cathode (○---○---○) and 1.0 M LiAlCl_4 in thionyl chloride with a calcium anode and SAB cathode (●---●---●). Both cells were discharged at 15 mA cm^{-2} at 25°C . Vapour pressure datum points pertain to the right hand vapour pressure ordinate.

between SOCl_2 and the cation. The interaction between the SOCl_2 dipole and the metal ion with polarizability ' α ' will determine if SO_2 can displace a solvent molecule and thereby become complexed with the metal ion. The interaction energy, ϕ_{av} , can be related to α from ref 9

$$\phi_{\text{av}} = -\alpha\mu^2/\gamma^6 \quad (1)$$

where μ is the dipole moment of the SOCl_2 molecule and γ the average interaction distance. A high α value for a given ion leads to a stronger interaction with the solvent, and therefore to increased vapour pressures because of the reduced likelihood of disrupting the cation's solvation cage, which is essential to form an interaction with SO_2 . In Fig 11 the polarizabilities of the four metal ions tested as tetrachloroaluminates (1.0 M in SOCl_2) are plotted against the percentage increase in vapour pressure to $0.9 E_{\text{avg}}$ for each discharge. To account for the different discharge times measured, the percentage vapour pressure increases are normalized to unit capacity (mA h^{-1}). The good linearity confirms the proportionality between ϕ_{av} and α , as ϕ_{av} is a measure of the inability of SO_2 to displace SOCl_2 , leading to an

TABLE 2

Discharge data for calcium-anoded cells (15 mA cm⁻² rate) with various supporting electrolytes in thionyl chloride at 25 °C
Polarizability data for tetrachloroaluminate cations are taken from ref 8

Electrolyte (1.0 M in SOCl ₂)	E_{avg} (V)	Capacity to $0.9 E_{avg}$ (mA h)	Increase in vapour pressure to $0.9 E_{avg}$ (%)	Increase in vapour pressure normalized to unit capacity (%)	Polarizability of cation (10^{-24} cm ³)
LiAlCl ₄	2.42	21.90	11	0.50	0.03
NaAlCl ₄	2.30	4.95	4	0.80	0.24
Cs ₂ (AlCl ₄) ₂	2.46	12.40	16	1.29	0.60
Sr ₂ (AlCl ₄) ₂	2.42	18.00	31	1.72	0.90

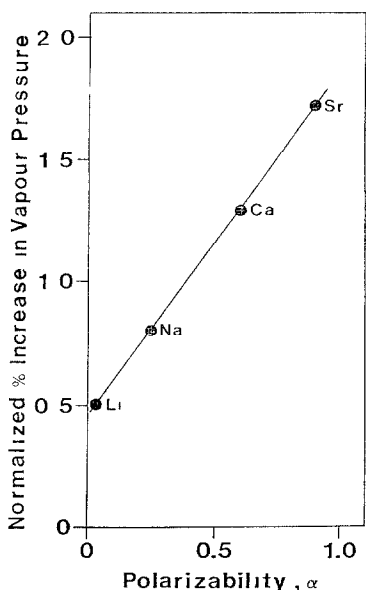


Fig 11 Relationship between cationic polarizability, α , in a solvate of the type $M(\text{SOCl}_2)_x^{n+}(\text{AlCl}_4)_n^-$ and % increase in vapour pressure normalised to unit capacity during discharge at 15 mA cm^{-2} to $0.9 E_{\text{avg}}$ for calcium-anoded thionyl chloride cells with a variety of tetrachloroaluminate supporting electrolytes

increase in vapour pressure The superior ability of lithium ions to complex with SO_2 is demonstrated in a calcium-anoded cell containing LiAlCl_4 . There is clearly a case for adding PCl_5 , or provision of a pressure vent in calcium/thionyl chloride cells, with $\text{Ca}(\text{AlCl}_4)_2$ as supporting electrolyte. Cells with SO_2 already present to increase electrolyte conductivity [10] are clearly not amenable to PCl_5 addition and venting should be considered.

Unfortunately, the use of an LiAlCl_4 supporting electrolyte in calcium-anoded cells removes one of the important safety features of calcium cells in that it would be possible to plate lithium in the event of accidental charging. Low load voltages and capacities of cells containing NaAlCl_4 as supporting electrolyte clearly excludes it as an alternative to $\text{Ca}(\text{AlCl}_4)_2$. $\text{Sr}(\text{AlCl}_4)_2$ has recently been investigated [11, 12] as a possible alternative to $\text{Ca}(\text{AlCl}_4)_2$ as it is much less corrosive towards calcium and had a 50% higher capacity. Such gains may be of no consequence if its inability to control internal pressure is of the essence.

Conclusions

(1) Lithium tetrachloroaluminate forms complexes of the type $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+(\text{AlCl}_4)^-$ with SO_2 produced during cell discharge in thionyl chloride electrolytes.

(ii) The analogous calcium or strontium complexes are not so readily formed although use of sulphuryl chloride as solvent enhances complex formation with all the cations. This may be attributed to the dipole moment of sulphuryl chloride which is some 38% higher than that of thionyl chloride (1.81 D versus 1.45 D).

(iii) Calcium-anoded cells with calcium tetrachloroaluminate in thionyl chloride electrolytes either require venting or the addition of PCl_5 to control internal pressure generation.

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