INTERACTIONS OF SO_2 WITH $Ca(AlCl_4)_2$–SO_2Cl_2 ELECTROLYTE: RAMAN STUDIES

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Summary

Raman spectra of $Ca(AlCl_4)_2$–SO_2Cl_2 electrolytes with, and without, added SO_2 have been obtained and analyzed. Added SO_2 preferentially complexes with calcium cations. The altered solvation sheath surrounding calcium cations in the presence of added SO_2 improves ion transport and increases cathode life.

Introduction

The addition of soluble sulfur dioxide to oxyhalide electrolyte containing $Ca(AlCl_4)_2$ salt has been shown to improve specific conductivity and dramatically increase cell capacity in calcium based cells [1 - 4]. The detailed reasons why the addition of SO_2 to this electrolyte improves solution conductivity and cell performance has not been fully elucidated.

In order to understand the interactions of SO_2 with sulfuryl chloride electrolyte species better, Raman spectral studies on various sulfuryl chloride-based electrolytes were performed. The implications of our data may also apply to $Ca(AlCl_4)_2$–thionyl chloride electrolyte. We have recently reported on NMR studies of $Ca(AlCl_4)_2$–SO_2Cl_2 electrolytes [5]. Raman spectra have been successfully utilized to non-intrusively study $AlCl_3$–$SOCl_2$–LiCl systems [6, 7] and $LiAlCl_4/SOCl_2/SO_2$ systems [8, 9]. The following electrolyte solutions were studied:

SO_2Cl_2
$SO_2Cl_2 + SO_2$
1 M $AlCl_3$–SO_2Cl_2
1 M $AlCl_3$–$SO_2Cl_2 + SO_2$
1 M $Ca(AlCl_4)_2$–SO_2Cl_2
1 M $Ca(AlCl_4)_2$–$SO_2Cl_2 + SO_2$

For each solution, we measured the Raman spectrum from 200 cm^{-1} to 1300 cm^{-1} and analyzed spectral differences of solutions with, and

without, added SO_2. In each case, when SO_2 was added, the electrolyte was saturated at room temperature with SO_2. Since Raman spectra from 200 cm^{-1} to 1100 cm^{-1} for these solutions do not show any major structural differences, only the 1100 - 1300 cm^{-1} spectral region will be discussed. We used 1 M concentrations in these studies in order to simulate concentrations used in practical cells.

Experimental

Crystalline $CaCl_2$ and sublimed $AlCl_3$ were purchased in ampoules sealed under argon from Anderson Physics, Urbana, IL. Anhydrous SO_2 was obtained from Matheson Gas Co., Rutherford, NJ. Sulfuryl chloride from E.M. Industries, Cherry Hill, NJ was distilled over lithium strips and stored in threaded pressure tubes in an argon-filled dry box (<10 ppm H_2O). All solution preparations were conducted in the argon-filled dry box. Solutions were placed in 1 cm glass NMR tubes that had been adapted with a stopcock and glass joint, attached to a vacuum line and frozen with liquid nitrogen. Then, while an active vacuum was applied, the tubes containing the frozen samples were sealed with a flame. Room temperature Raman spectra were obtained by Drs Adar and Armalino of Instruments S.A., Metuchen, NJ using a U-1000 Laser Raman system set with 400 μm slit widths. The 60 mW 6471A argon ion laser line was used for excitation. Integration times ranged from 0.25 to 1.0 s per wavenumber.

Results and discussion

(a) SO_2Cl_2

Figure 1 shows Raman spectra of pure SO_2Cl_2 with, and without, added SO_2. Raman spectra of sulfuryl chloride agreed well with published literature data [10]. An SO_2Cl_2 band appeared at 1183 cm^{-1} and we assigned a small peak at 1145 cm^{-1} to SO_2 generated by self dissociation of SO_2Cl_2 [11]. Addition of soluble SO_2 to SO_2Cl_2 did not change the position of these bands, but the 1145 cm^{-1} SO_2 band became more intense. If we assume that room temperature solubility of SO_2 in sulfuryl chloride is similar to the approximately 3 M that had been measured in pure thionyl chloride [12], then by measuring observed peak height ratios of the 1145 cm^{-1} SO_2 band to the 1183 cm^{-1} SO_2Cl_2 band in both pure and SO_2 saturated SO_2Cl_2, the amount of free SO_2 present in pure SO_2Cl_2 due to self dissociation can be estimated. This calculation yields an SO_2 concentration in pure sulfuryl chloride of 0.33 M which translates into an SO_2Cl_2 self dissociation equilibrium constant of 0.009. This value is in agreement with the value of 0.01 previously measured by Binder et al. [11]. Since the molarity of pure sulfuryl chloride is 12.37 M, the 0.33 M SO_2 (and Cl_2) formed implies that approximately 2.6% of the sulfuryl chloride is dissociated.
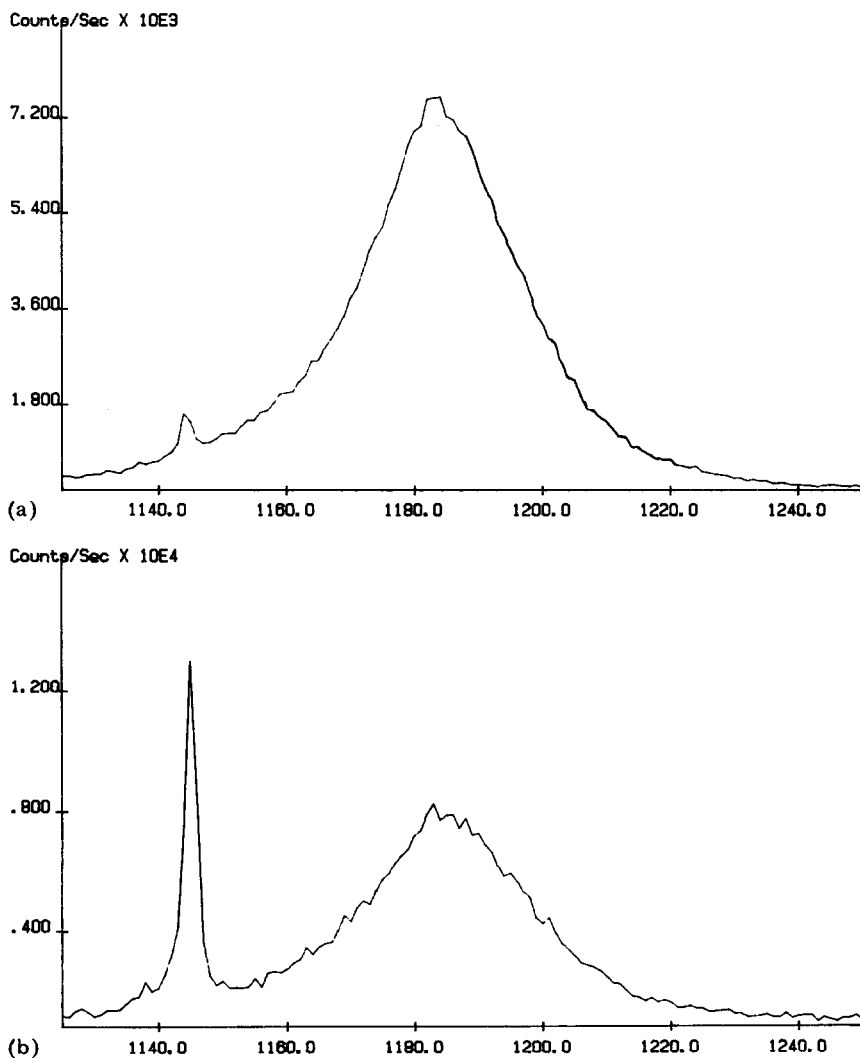
Counts/Sec X 10E3

7.200

5.400

3.600

1.800

(a)　　　1140.0　　　1160.0　　　1180.0　　　1200.0　　　1220.0　　　1240.0

Counts/Sec X 10E4

1.200

.800

.400

(b)　　　1140.0　　　1160.0　　　1180.0　　　1200.0　　　1220.0　　　1240.0

Fig. 1. Raman spectra of (a) pure SO_2Cl_2 and (b) SO_2Cl_2 saturated with SO_2.

(b) AlCl₃-SO₂Cl₂

(b) A lCl₃-SO₂Cl₂

Figure 2 shows Raman spectra of a 1 M $AlCl_3$-SO_2Cl_2 solution with, and without, added SO_2. The Raman spectra of 1 M $AlCl_3$-SO_2Cl_2 solution was very noisy because of light scattering from the highly concentrated electrolyte, and the large amount of background fluorescence probably due to the presence of a charge-transfer complex species such as $AlCl_4$-SO_2Cl^+ in solution. Although addition of SO_2 appeared to decrease the background fluorescence, the positions of the SO_2 peak and SO_2Cl_2 band in this electrolyte are essentially unchanged from that found in pure SO_2Cl_2. The new peak appearing at approximately 1237 cm^{-1} in $AlCl_3$-SO_2Cl_2 electrolyte contain-
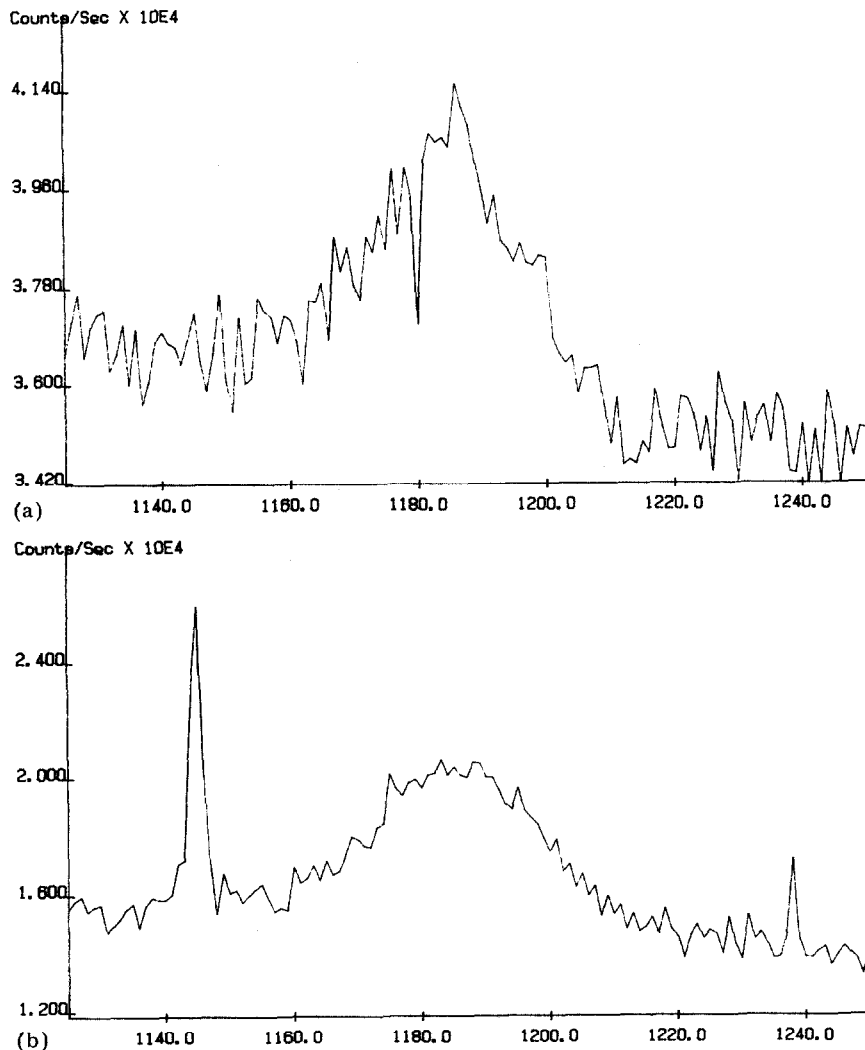
Fig. 2. Raman spectra of (a) 1 M AlCl$_3$–SO$_2$Cl$_2$; (b) 1 M AlCl$_3$–SO$_2$Cl$_2$ saturated with SO$_2$.

ing added SO$_2$ may be due to an SO stretch. Thus, although there may be some interaction between SO$_2$ and AlCl$_4^-$SO$_2$Cl$^+$ species formed in solution, they are relatively weak. These conclusions are in agreement with NMR data on these solutions [5].

(c) Ca(AlCl$_4$)$_2$–SO$_2$Cl$_2$

Figure 3 shows Raman spectra of Ca(AlCl$_4$)$_2$–SO$_2$Cl$_2$ electrolyte by itself and also when saturated with SO$_2$. Ca(AlCl$_4$)$_2$–SO$_2$Cl$_2$ exhibits the same SO$_2$Cl$_2$ band seen in other solutions. The electrolyte containing added SO$_2$ was clearly different. In addition to the SO$_2$ peak at 1145 cm^{-1}, an addi-
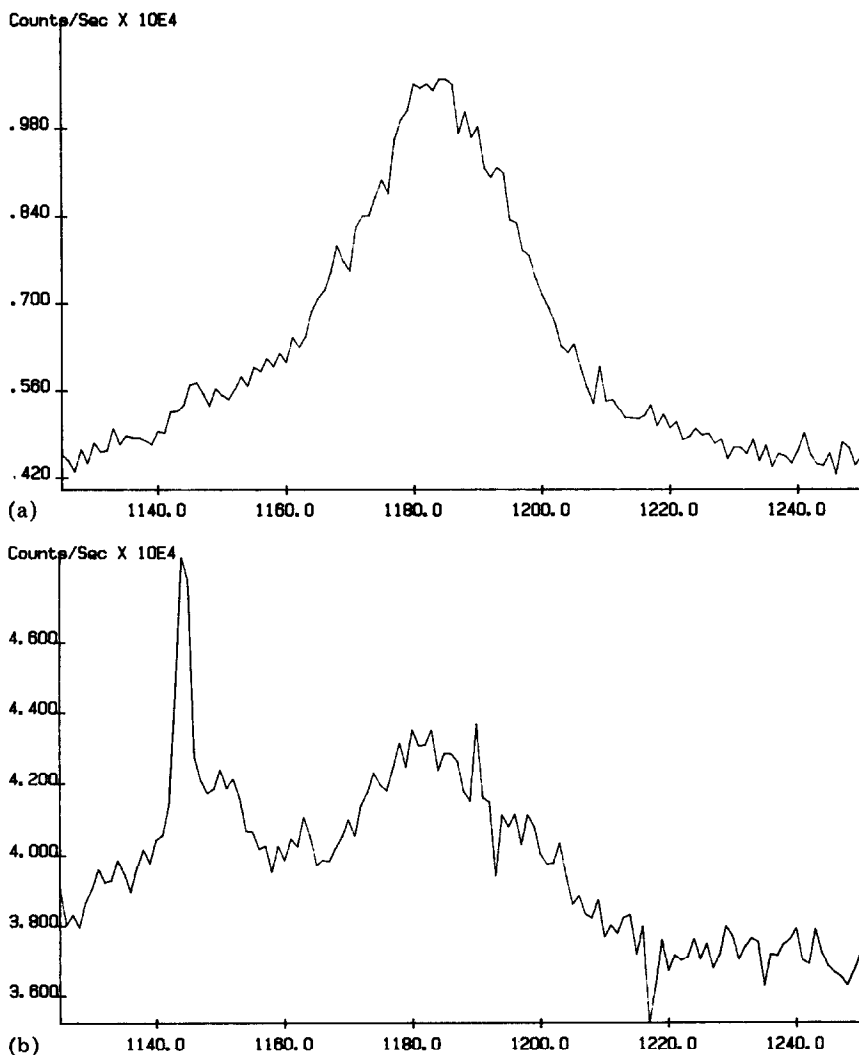
Counts/Sec X 10E4

(a)

Counts/Sec X 10E4

(b)

Fig. 3. Raman spectra of (a) 1 M Ca(AlCl₄)₂–SO₂Cl₂; (b) 1 M Ca(AlCl₄)₂–SO₂Cl₂ saturated with SO₂.

tional broad band was noticeable at 1155 cm⁻¹. This new band is similar to the 1157 cm⁻¹ band which appeared in LiAlCl₄–SOCl₂ solutions containing added SO₂, which was attributed to a complex formed between SO₂ and Li⁺ cations in which three SO₂ molecules solvate each Li⁺ cation [8, 9]. In a similar manner, in our solutions, we can assume that SO₂ molecules preferentially solvate Ca²⁺ cations.

A simple model can be used to explain the conductivity increase accompanying SO₂ addition to Ca(AlCl₄)₂–SO₂Cl₂ electrolyte. In baseline electrolyte, SO₂Cl₂ molecules normally solvate Ca²⁺ cations, with the partially negative charge on the oxygen atoms from SO₂Cl₂ pointing inward towards

the Ca^{2+} cation. In SO_2 saturated electrolyte, the smaller SO_2 molecules replace SO_2Cl_2 molecules in the solvation sheath. As the composition of this solvation layer changes, this zone of molecules surrounding the Ca^{2+} cation changes in size and thus Ca^{2+} cation mobility can increase. Increased ion mobility translates into increased electrolyte conductivity, less *IR* losses in actual cells, and thus higher operating load voltages. All of these effects have been observed in calcium cells [1, 2, 5].

Similarly, the increase in porous carbon cathode capacity observed when cathodes are discharged in calcium-based electrolytes saturated with SO_2 [2] can also be explained. In SO_2 saturated electrolyte, SO_2 bound to Ca^{2+} is transported through· the electrolyte to cathode sites where Ca^{2+} cations combine with Cl^- anions (generated at the cathode by solvent reduction) to form insoluble $CaCl_2$. When this occurs, SO_2 is now freed from the cation and cracks the normally glassy $CaCl_2$ discharge product. Since porous carbon cathode capacity is limited by formation of this impermeable layer, cracking of $CaCl_2$ by escaping SO_2 allows continued ion flow into the cathode interior, allows more complete cathode utilization, and thus extends cathode capacity. SEM of porous carbon cathodes discharged in $Ca(AlCl_4)_2$–thionyl chloride electrolyte saturated with SO_2 show a less glassy, more cracked structure than cathodes discharged in electrolyte without added SO_2.

It is interesting to note that, although pure SO_2Cl_2 or SO_2Cl_2 solutions containing SO_2 do not fluoresce when excited at 465 nm, 1 M solutions of $AlCl_3$–SO_2Cl_2 or $Ca(AlCl_4)_2$–SO_2Cl_2 show significant fluorescence out to 660 nm with a fluorescence peak at about 520 nm. This fluorescence increases by about 20% when these solutions are saturated with SO_2. Apparently, these solutions undergo a considerable amount of fluorescence self absorption. Addition of SO_2 dilutes the effective electrolyte concentration and thus increases the observed fluorescence from the solutions.

Conclusion

Improvements in cathode capacity and electrolyte conductivity observed when SO_2 is added to $Ca(AlCl_4)_2$–SO_2Cl_2 solutions are attributed to complexation to Ca^{2+} by added SO_2. The SO_2 preferentially complexes with Ca^{2+} and serves to improve Ca^{2+} transport by substituting for SO_2Cl_2 species.

Acknowledgements

References

1 C. W. Walker, Jr., W. L. Wade, Jr., M. Binder and S. Gilman, *32nd Int. Power Sources Symp., Cherry Hill, NJ, 9 - 12 June, 1986.*

2 C. W. Walker, Jr., W. L. Wade, Jr., M. Binder and S. Gilman, *J. Electrochem. Soc., 133* (1986) 1555.

3 E. Peled, *32nd Int. Power Sources Symp., Cherry Hill, NJ, 9 - 12, June, 1986.*

4 E. Peled, E. Elster, R. Tulman and J. Kimel, *J. Power Sources, 14* (1985) 93.

5 C. W. Walker, Jr., W. L. Wade, Jr. and M. Binder, *J. Electrochem. Soc., 135* (1988) 2471.

6 R. C. McDonald and F. W. Dampier, *Final Rep. Contract N60921-81-R-0190, Jan. 1983.*

7 P. A. Mossier-Boss, S. Szpak and J. J. Smith, *Spring Meeting of the Electrochem. Soc., Philadelphia, PA, 1987.*

8 Y. Bedfer, J. Corset, M. C. Dhamelincourt, F. Wallart and P. Barbier, *J. Power Sources, 9* (1983) 267.

9 M. C. Dhamelincourt, F. Wallart, P. Barbier, G. Mairesse and P. Descroix, *J. Power Sources, 14* (1985) 77.

10 R. J. Gillespie and E. A. Robinson, *Can. J. Chem., 39* (1961) 2171.

11 M. Binder, C. W. Walker, Jr., W. L. Wade, Jr. and S. Gilman, *Fall Meeting of the Electrochem. Soc., San Diego, CA, Oct. 19 - 24, 1986.*

12 K. A. Klinedinst and M. L. McLaughlin, *J. Chem. Eng. Data, 24* (1979) 203.