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Speciation in the $AlCl_3/SO_2Cl_2$ Catholyte System

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The fundamental chemical behavior of the $AlCl_3/SO_2Cl_2$ catholyte system was investigated using ^{27}Al NMR spectroscopy, Raman spectroscopy, and single-crystal X-ray diffraction. Three major Al-containing species were found to be present in this catholyte system, where the ratio of each was dependent upon aging time, concentration, and/or storage temperature. The first species was identified as $[Cl_2Al(\mu\text{-}Cl)]_2$ in equilibrium with $AlCl_3$. The second species results from the decomposition of SO_2Cl_2 which forms Cl_2(g) and SO_2(g). The SO_2(g) is readily consumed in the presence of $AlCl_3$ to form the crystallographically characterized species $[Cl_2Al(\mu\text{-}O_2SCl)]_2$ (**1**). For **1**, each Al is tetrahedrally (T_d) bound by two terminal Cl and two μ-O ligands whereas, the S is three-coordinated by two μ-O ligands and one terminal Cl. The third molecular species also has T_d-coordinated Al metal centers but with increased oxygen coordination. Over time it was noted that a precipitate formed from the catholyte solutions. Raman spectroscopic studies show that this gel or precipitate has a component that was consistent with thionyl chloride. We have proposed a polymerization scheme that accounts for the precipitate formation. Further NMR studies indicate that the precipitate is in equilibrium with the solution.

Introduction

A new generation of batteries is necessary to meet power and energy requirements of the smaller electronic devices demanded by both the public and private sectors, as well as the ability to meet these needs after prolonged (years) storage.[1] Due to the portability of these new devices, progressively diverse and increasingly harsh environments are being encountered. Therefore, it is necessary that the battery operate over a large temperature range during storage as well as after storage under even more severe environmental conditions. While numerous systems have been investigated, batteries using the catholyte system of aluminum chloride ($AlCl_3$) dissolved in sulfuryl chloride (SO_2Cl_2) have maintained viability at both the higher and lower temperatures (−50 to +125 °C).[2−4] A catholyte system is one where a liquid operates as both the cathode and electrolyte. Enhancing the long-term stability of the inherently unstable $AlCl_3/SO_2Cl_2$ catholyte system is necessary to make this a useful material. To accomplish this, it is necessary to understand the various chemical changes that are occurring in the reaction mixture.

Several studies are available concerning the chemical behavior associated with both $AlCl_3$ and SO_2Cl_2 independently, but there are little data readily available for the combined system.[2−4] Glidewell reported that $[SCl_3]^+[AlCl_4]^-$ was the active chlorinating species in the complex $SO_2Cl_2-S_2Cl_2-AlCl_3$ system.[4] Additional reports indicate that molecular ionic compounds are formed upon mixing thionyl chloride ($SOCl_2$) and $AlCl_3$, some of which are proposed to be $[SOCl]^+[AlCl_4]^-$,[5] $Cl_2SO-AlCl_3$,[6] and $Cl(O)SCl-AlCl_3$.[7] However, we can find no report that establishes an interaction between SO_2Cl_2 and $AlCl_3$.[2−4]

Therefore, we undertook the systematic study of the chemical behavior of the $SO_2Cl_2/AlCl_3$ catholyte solution as a stand-alone system in order to reduce the overall complexity of the problem, but also because this configuration most closely resembles a reserve battery. In this case the catholyte is held in a separate reservoir during storage, and on battery activation the reservoir is breached, allowing catholyte to

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mix and flood the remaining chemical constituents of the battery. The information garnered will assist in understanding and improving battery performance over extended time frames and in identifying storage protocols that extend battery shelf life. This report details the observed chemical changes the $SO_2Cl_2/AlCl_3$ catholyte solution underwent as determined by ^{27}Al NMR spectroscopy, Raman spectroscopy, and single-crystal X-ray diffraction, which identified a unique intermediate species $[Cl_2Al(\mu\text{-}O_2SCl)]_2$ (**1**)[8]—the first adduct ever isolated for this catholyte system. The synthesis of this compound and the other species characterized in this system are discussed below.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques. The SO_2Cl_2 (MCB Reagents), $AlCl_3$ (99.999%, Aldrich), and $SO_2(g)$ (TriGas, Inc.) were opened and used as received, in a glovebox under an argon atmosphere. The various solution concentrations were prepared by dissolving preweighed $AlCl_3$ into measured amounts of SO_2Cl_2. Water was added via syringe to the appropriate samples. All samples were prepared under argon atmospheres by placing aliquots of the appropriate solutions into Pyrex NMR tubes and then flame-sealing the tube under vacuum.

The solution ^{27}Al NMR spectra were obtained on a Bruker DRX400 instrument operating at 104.2 MHz using a 5 mm broad band probe operating at 298 K. Typical acquisition conditions included between 16 and 64 scans averaging, 1 s recycle delay, 8 K complex points using a 600 ppm spectral width. Chemical shifts were referenced to a secondary standard 1 M $Al[H_2O]_6^{3+}$, $\delta = 0.0$ ppm.

The Raman spectra were obtained using a triple spectrograph and charge-coupled-device detector for dispersing and recording the Raman-scattered light. A 90° scattering configuration and a 785 nm excitation laser were used to obtain Raman spectra from the solutions sealed in NMR tubes. For gelled species in sealed containers, we employed a 458 nm excitation laser and a microscope accessory in a 180° scattering configuration.

$[Cl_2Al(\mu\text{-}O_2SCl)]_2$ (1). In a glovebox, $AlCl_3$ (2.00 g, 14.9 mmol) was added to a vial of SO_2Cl_2 (~10 mL) to form an ~1.5 M solution. The yellow mixture was stirred for 12 h and became progressively darker in color. After sitting for an extended period of time, the resulting brown solution was placed into a freezer (−25 °C) for 2 days. Clear crystals were observed at low-temperature; however, any attempt to isolate them at room temperature resulted in their melting, which prevented obtaining bulk analytical data for **1**. Crystals suitable for X-ray diffraction were obtained by pouring off the mother liquor and placing the vial containing the crystalline material in an ice bath prior to manipulating them on a homemade, liquid nitrogen cooled coldfinger.

X-ray Crystal Structure Information.[9] The crystal was mounted onto a thin glass fiber under an atmosphere of flowing liquid N_2, and immediately placed under a liquid N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT Version 6.01 software. The structure refinement was performed using XSHELL 3.0 software. The data were corrected for absorption using the SADABS program within the SAINT software package.

Discussion

Due to the dearth of information concerning the species present in the $AlCl_3/SO_2Cl_2$ solution and our interest in using this catholyte system, we undertook a series of analytical investigations to elucidate the chemical speciation of this system. Several key conditions were varied: (i) the amount of water present, (ii) the $AlCl_3$ concentration, (iii) solution storage or aging temperature, and (iv) the solvent. The changes in this system were analyzed using NMR and Raman spectroscopies in conjunction with single-crystal X-ray diffraction.

Precursor Materials. Our initial investigations focused on the properties of the starting materials in solution. All attempts to purify the precursors only resulted in the inclusion of additional contaminants or no improvement in purity. Double sublimation of an alternative source of $AlCl_3$ (98%) did not remove the fluorescent impurities that dominated the region of the Raman spectrum of interest to us; however, the as-received 99.99% pure materials did not possess these fluorescent contaminants. During distillation of SO_2Cl_2, corrosive attack by the solvent introduced organic species (i.e., decomposition products of silicon grease, Tygon tubing) into the distilled material. Therefore, the reagents were used as received but opened and handled only under an argon atmosphere.

The ^{27}Al NMR chemical shift is directly related to the coordination of the Al metal centers. $AlCl_3$ dissolved in toluene-d_8 revealed a broad ^{27}Al singlet (250 Hz) at $\delta = +102$ ppm. This chemical shift is consistent with tetrahedrally (T_d) bound Al metal centers.[10−13] The large line width suggests either changes in the electrical field gradient or an increase in the correlation time of these field gradient fluctuations due to solvent interactions, increased aggregation of the molecular species, or chemical exchange with other Al-containing species in solution. The observed signal in our sample is consistent with a T_d Al species found for $AlCl_3$ in nonpolar solvents and melted $AlCl_3$, instead of the nominal octahedral coordination Al species ($\delta \sim 0$ ppm) observed for the room-temperature solid-state $AlCl_3$ structure.[10−13] Proposed T_d species for this solution species include Al_2Cl_6 or $AlCl_4^-$, which are known to be relatively insensitive to concentration and temperature but have a ^{27}Al chemical shift that is solvent-dependent.[12,13] The ^{27}Al chemical shift of the $Al_2Cl_7^-$ dimer is reported to be $\delta = +116$ ppm.[14] For

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[8] Cambridge Crystallographic Data Centre, Cambridge, United Kingdom, www.ccdc.cam.ac.uk, was searched using ConQuest v 5.25 (April 2004).

[9] The listed versions of SAINT, SMART, XSHELL, and XPOW in SHELXTL and SADABS Software from Bruker Analytical X-ray Systems Inc., (Madison, WI) were used in the analysis.

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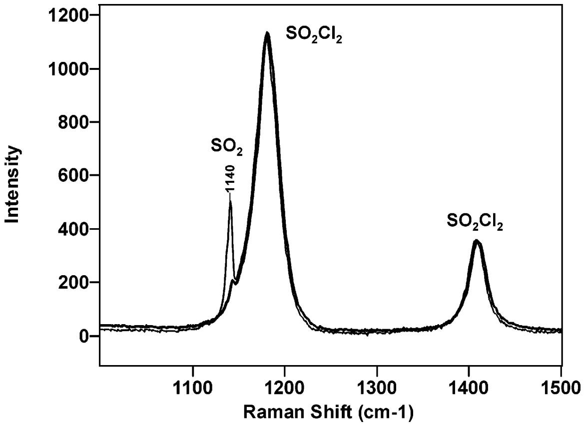

Figure 1. Raman spectra of SO_2Cl_2 prior to aging (solid line) and after aging at 74 °C for 2 weeks (dotted line).

unassociated or non-exchanging $AlCl_4^-$ complexes line widths on the order of only a few hertz have been reported ranging from +101 to +108 ppm.[15] Therefore, we propose that the observed line width is due to the equilibrium between the monomer and Al_2Cl_6 dimer (eq 1), wherein the T_d-coordinated Al dimer is the major species present.[12,13]

$$2AlCl_3 \rightleftarrows [Cl_2Al(\mu\text{-}Cl)]_2 \tag{1}$$

Because of the limited number of NMR handles available for SO_2Cl_2, Raman studies were undertaken to elucidate its aging behavior. For a flame-sealed NMR tube of SO_2Cl_2, after 2 weeks at 74 °C, we observed the in-growth of a peak at 1142 cm^{-1}, which is consistent with SO_2(g) generation. The Raman spectra are shown in Figure 1. Observed at 500−550 cm^{-1}, but not shown, are bands associated with Cl_2(g) that developed in a manner consistent with the generation of SO_2(g). The Raman spectra indicate that SO_2Cl_2 decomposes as shown in eq 2.[16]

$$SO_2Cl_2 \rightleftarrows SO_2(g) + Cl_2(g) \tag{2}$$

Catholyte Solution. Upon addition of $AlCl_3$ to a clear SO_2Cl_2 solution, the reaction mixture turns pale yellow. Of initial interest was whether H_2O (0, 100, 300, 500 ppm) effected the molecular speciation. Based on ^{27}Al NMR data from $AlCl_3/SO_2Cl_2$ solutions to which up to 500 ppm of water had been added, no change in the number or types of Al species present was observed, and none of the observed peaks were consistent with the previously identified hydrolysis species of $AlCl_3$.[13] The lack of significant Al hydrolysis in the $AlCl_3/SO_2Cl_2$ catholyte solution is not unexpected since the chemistry associated with SO_2Cl_2 (the major component) would necessarily dominate. Water addition to SO_2Cl_2 has been found to follow the reactions shown in eqs 3 and 4,[17−19] which would have little effect on the Al species present, especially at the part per million scale. Therefore, water at up to 500 ppm does not significantly affect the aging of the catholyte system; nor does it play a role in the reactions associated with the active Al metal centers.

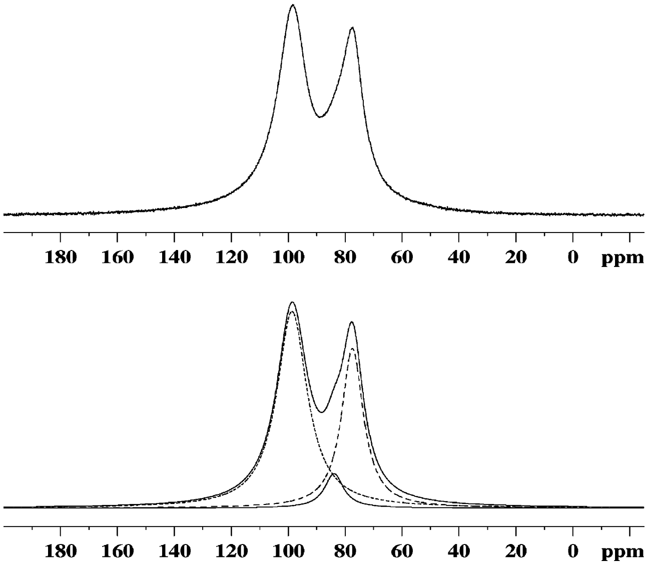

Figure 2. Solution ^{27}Al NMR spectrum of (a) catholyte solution at room temperature and (b) the simulated spectral deconvolution.

$$SO_2Cl_2 + 2H_2O \rightleftarrows H_2SO_4 + 2HCl \tag{3}$$

$$SO_2Cl_2 + H_2SO_4 \rightleftarrows 2ClSO_3H \tag{4}$$

Studies on the effect of $AlCl_3$ concentration on molecular speciation were undertaken by varying the amounts of $AlCl_3$ added to the same volume of SO_2Cl_2. It was found that the same Al species were present in each sample but at different relative amounts. The ratio of these species was influenced by aging time, temperature of reaction, and $AlCl_3$ concentration. Since the two major variables of interest (humidity and concentration) appeared to have little effect on the identity of the molecular species present, our efforts focused on understanding the aging of the catholyte without added water and with the $AlCl_3$ concentration normally used in battery operation.

Aging of Catholyte. Over time, the solution ^{27}Al NMR revealed the presence of at least three different types of T_d-bound Al species present in the catholyte (see Figure 2) at $\delta = +99.0$ (line width = 1400 Hz), +82.4 (1630 Hz), and +77.2 ppm (820 Hz). The decreasing ^{27}Al chemical shift of these species is consistent with a T_d Al centers gaining more oxygen character.[11,13] With increased temperature and aging time, the relative concentrations of the smaller chemical shift (more shielded) Al species increased. The large line widths again suggest that these different Al species are involved in solvent complexes or exchange processes.

Two-dimensional ^{27}Al NMR exchange experiments were pursued to measure the interchange between these different Al species (an example is shown in Figure 3). The Al species comprising the two dominant peaks at $\delta \sim +101$ and +80 ppm were found to be in rapid exchange (~1 ms), supporting the argument of an equilibrium between complexes in

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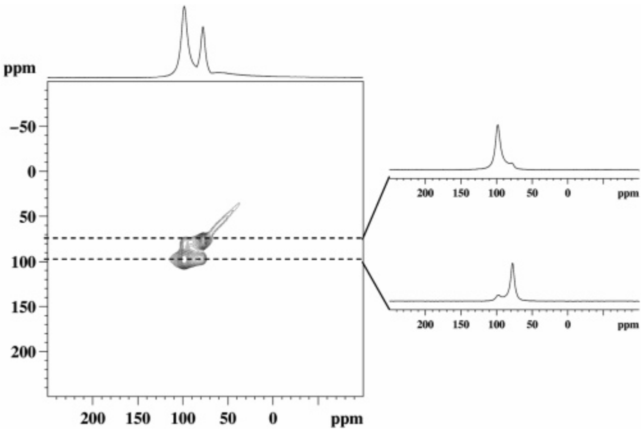

Figure 3. 2D ^{27}Al NMR exchange spectrum of catholyte. The broad resonance at ~50 ppm is due to probe background.

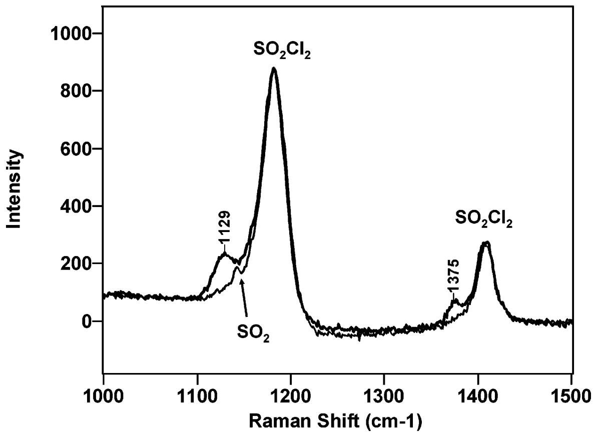

Figure 4. Raman spectra of SO_2Cl_2/1.5 M $AlCl_3$ prior to aging (solid line) and after aging at 74 °C for 2 weeks (dotted line).

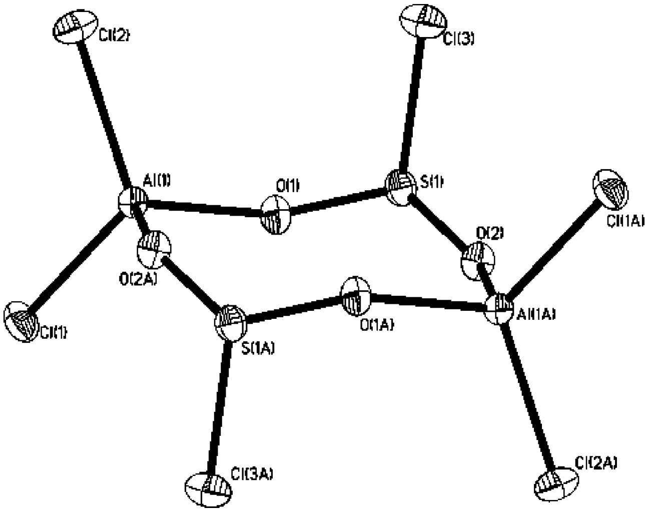

Figure 5. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at 30% level.

solution. Exchange with the minor species at ~+85 ppm is not readily apparent in the 2D ^{27}Al exchange experiment due to the low concentration of this species and the large line widths of the other dominant resonances.

In an effort to identify some of these Al species, we investigated the low-temperature behavior of $AlCl_3$ in SO_2Cl_2 soon after its addition. This was undertaken by generating a sample of the catholyte, sealing it in a glass tube, and freezing it in liquid nitrogen. The sample was transferred to a cold NMR probe and was slowly warmed to room temperature. The single ^{27}Al NMR resonance observed at δ +101 ppm (identical to $AlCl_3$ in tol-d_8) is assigned to the T_d dinuclear species Al_2Cl_6 in eq 1.

In the freshly prepared $SO_2Cl_2/AlCl_3$ solution Raman spectroscopy (Figure 4) revealed the presence of a species with Raman bands at 1129 and 1375 cm^{-1}. These bands are not present in Raman spectra of SO_2Cl_2 solutions without $AlCl_3$ (Figure 1) and are believed to be due to an adduct between SO_2Cl_2 and $AlCl_3$. This is in contrast to Walker and co-workers who report that the spectrum remained essentially unchanged from pure SO_2Cl_2; however, due to the very high noise produced from a large amount of background fluorescence,[16] the authors may not have been able to observe the subtle changes noted in this report. After 2 weeks of aging at 74 °C, these bands disappeared from the Raman spectrum of the $SO_2Cl_2/AlCl_3$ solution (Figure 4). Further, the evolution of $SO_2(g)$ was significantly reduced in the SO_2Cl_2 solution containing $AlCl_3$ (1142 cm^{-1}, Figure 4) compared to the solution containing SO_2Cl_2 only (Figure 1). In the SO_2Cl_2 solution containing $AlCl_3$, $AlCl_3$ either consumes any $SO_2(g)$ generated or reacts with species that otherwise would evolve $SO_2(g)$. Cooling a sample that had been aged yielded crystalline material which was identified as $[Cl_2Al(\mu\text{-}O_2SCl)]_2$ (**1**) and is shown in Figure 5.

Compound 1. Compound **1** consists of a cyclic dimer with μ-O linking the S and the main group metal Al. The T_d-bound Al metal centers have two terminal Cl, whereas the trigonal S has one terminal Cl. The equal distances noted for **1** imply that the double-bonded oxygen is dispersed over the two S−O bonds. The Al−Cl and Al−O bonds are consistent with literature values.[8,20−27] The constructs of **1** are unique[8] and can either represent coordination of SO_2Cl_2 with loss of Cl_2 or as an SO_2 insertion into an Al−Cl bond product. Table 1 lists the collection data parameters for compound **1**. Due to the consumption of the SO_2, as suggested by the Raman spectra, the latter explanation is favored. Compound **1** is not stable at high temperature and will convert to $AlCl_3$ (as confirmed by solid-state NMR spectroscopy experiments) upon washing with any solvent or drying in vacuo. This implies a reversible insertion of $SO_2(g)$ and suggests the equilibrium shown in eq 5. The solid-state ^{27}Al MAS NMR spectrum (not shown) of **1** showed two peaks at δ +101 and +96.5 ppm. Due to the rapidity of decomposition (gas evolution) it is not unexpected

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Table 1. Data Collection Parameter for **1**

compd	**1**
chem formula	$Al_2Cl_6O_4S_2$
fw	394.78
temp (K)	168(2)
space group	triclinic $P\bar{1}$
a (Å)	6.188(7)
b (Å)	7.351(8)
c (Å)	7.816(8)
α (deg)	94.202(17)
β (deg)	106.616(16)
γ (deg)	109.251(15)
V (Å^3)	316.0(6)
Z	1
D_{calcd} (Mg/m^3)	2.074
μ(Mo Kα) (mm^{-1})	1.810
R1^a (%) (all data)	2.94 (3.71)
wR2^b (%) (all data)	7.32 (7.68)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o|^2)^2]^{1/2} \times 100$.

to see the peak associated with the Al_2Cl_6 equilibrium present. The +96.5 ppm resonance is similar to the +94 ppm resonance assigned to the $AlCl_3{\cdot}xSO_2$ observed in dialkyl sulfone mixtures.[11]

$$\text{(xs) } SO_2(g) + Al_2Cl_6 \rightleftarrows [Cl_2Al(\mu\text{-}O_2SCl)]_2 \qquad (5)$$

To verify the insertion/deinsertion of $SO_2(g)$, the synthesis of **1** was undertaken by bubbling $SO_2(g)$ through $AlCl_3$ in toluene. Undissolved $AlCl_3$ was instantly solubilized, and the resulting crystals isolated proved to be **1**. Again, studying the early species formed by freezing an NMR tube of $AlCl_3$ with condensed $SO_2(g)$ and allowing it to slowly warm to room temperature allowed some insight into the reaction behavior of the $AlCl_3$. ***Caution:*** *Extreme caution must be used during condensation of $SO_2(g)$ to avoid overpressurization of the NMR tube.* Initially the Al_2Cl_6 resonance at +102 ppm was observed; however an $SO_2(g)$ adduct, which grows in over time, was also observed at a resonance of ~+80 ppm. This ^{27}Al NMR feature is consistent with the assignment discussed for the original crystal of **1**. The ^{27}Al NMR spectrum of this compound has resonances that are similar but not identical to what was observed for the original catholyte mixture. Therefore, the SO_2Cl_2 leads to additional alternative reactivity (i.e., there is more to the reaction than the interaction of $SO_2(g)$ and $AlCl_3$).

Precipitate. As the catholyte solution ages, ^{27}Al NMR studies indicate that the soluble species become more oxo in nature until eventually a precipitate forms. This gellike precipitate, present in aged solutions in both NMR tubes and battery reservoirs, was analyzed by micro-Raman spectroscopy. Bands due to SO_2Cl_2 entrapped in the precipitate were subtracted from the as-obtained spectra, and with a typical difference Raman spectrum being shown in Figure 6. The derivative-like feature(s) in the difference spectrum of Figure 6 are related to incomplete removal of the SO_2Cl_2 bands. Bands due to dissolved Cl_2 are also present. Interestingly, the remaining features in the difference spectrum are similar to Raman bands from thionyl chloride ($SOCl_2$, top, Figure 6), indicating that the precipitate has features consistent with $SOCl_2$.

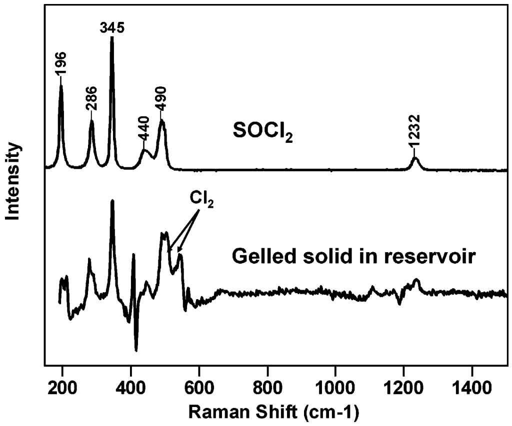


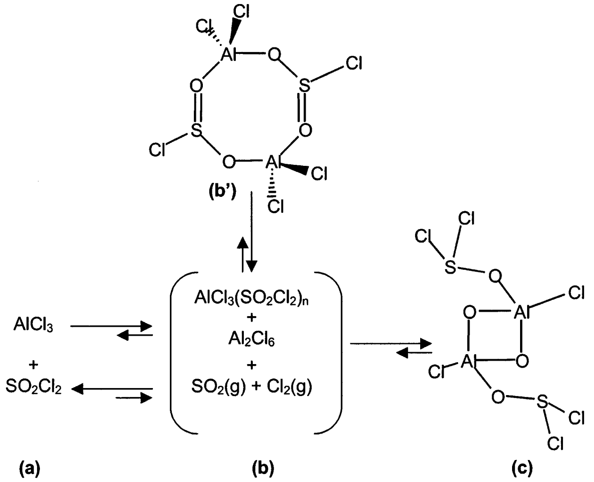
Figure 6. Raman spectrum of thionyl chloride ($SOCl_2$, top) and the difference spectrum (gelled solid minus SO_2Cl_2, bottom) from a battery reservoir.

Proposed Scheme of Catholyte Behavior. On the basis of the above data, we have proposed a general reactive pathway (Scheme 1) for the catholye $AlCl_3/SO_2Cl_2$ system. The initial mixture has several equilibria as shown in Scheme 1a,b. From this mixture a number of adducts could result. We have identified **1** (Scheme 1b′). Raman and NMR data indicate a great deal of ligand exchange, and molecular transformations are occurring for this system. An O−S bond in a compound like **1** may be broken followed by rearrangement of the freed O atoms (Scheme 1c). A simple Cl transfer forms a small dinuclear species with more oxo character and the $SOCl_2$ moiety noted above. Once formed, this precursor can start to cross-link (Scheme 2c) forming larger species (Scheme 2d). For this process a slight rearrangement of Al−O bonds results in larger oligomers. The degree that this rearrangement occurs will determine the solubility. For this mechanism, it should be noted that the Al atoms all remain T_d and adopt more oxo character. These changes are consistent with the analytical data collected on the catholyte system.

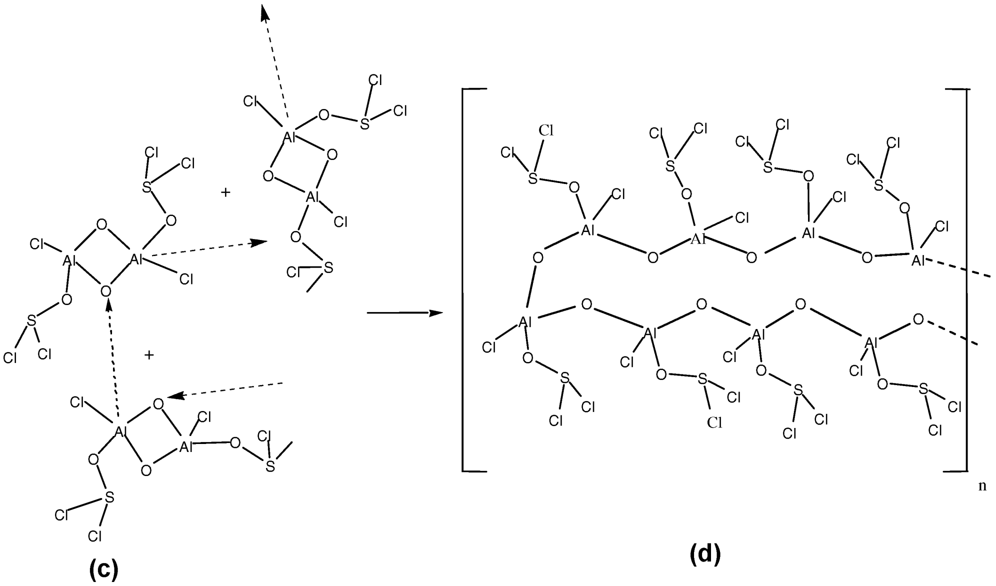
To study the precipitate, it was first necessary to generate a significant volume of material. Therefore, a sample of 1.5 M $AlCl_3$ in SO_2Cl_2 in a glass ampule under vacuum was sealed and heated to 120 °C overnight. A large volume of precipitate was observed; however, the sample was found to be under significant pressure even at room temperature (***Caution:*** *Great care must be taken in handling these samples due to the potential of explosion from the gas buildup*). Therefore, after cooling to room temperature, the sample was frozen in liquid nitrogen, transferred into the glovebox, opened, and allowed to slowly melt and de-gas. The mother liquor was decanted off from the off-white solid precipitate that formed. From the ^{27}Al solid-state NMR data (not shown) for this precipitate, it is readily apparent that the T_d coordination is no longer the dominant feature. The major species present now have octahedral (Oh) and trigonal-bipyramidal (tbp) geometries. The cross-linking of the smaller molecules would lead to polymers and eventually a precipitate (Scheme 2).

Investigation of the mother liquor lends some insight into the behavior of this precipitate. For the 24 h mother liquor

Scheme 1. Observed Chemistry of SO_2Cl_2 Catholyte Solution: (a) Initial Mixture, (b) Intermediate Solution, (b′) One Possible Adduct Isolated at Low Temperature (**1**), and (c) Precipitate Precursor



Scheme 2. Conversion from (c) Precipitate Precursor to (d) Precipitate or Gel



solution, the ^{27}Al NMR spectrum is similar to what was previously discussed. However, when compared to a sample that was heated for 168 h, Al_2Cl_6 was found to dominate the latter ^{27}Al NMR spectrum. This can only be accounted for if the precipitate is in equilibrium with the solution. That is, the Al_2Cl_6 should not spontaneously regenerate if the reaction is slowly and irreversibly forming precipitate; however, if the precipitate is being re-dissolved, the equilibrium would shift to the left and form the observed Al_2Cl_6 species.

Finally, it should be mentioned that the experimental approach used in these studies, namely, the (1) hermetically sealed vials, (2) temperatures, (3) concentrations, and (4) minor impurities and their relative amounts, closely approximate those used for storage of both the catholyte and the reserve battery itself, where the catholyte is held in a hermetically sealed container prior to battery activation. Consequently, the results of these studies are directly applicable to the problem of understanding and improving battery performance over extended time frames and in identifying storage protocols that extend battery shelf life.

Summary and Conclusion

The fundamental chemical behavior of the catholyte $AlCl_3/SO_2Cl_2$ system was investigated using a variety of analytical tools including Raman and ^{27}Al NMR spectroscopies and single-crystal X-ray diffraction. From these investigations, it was determined that all catholyte samples possessed the same chemical species in solution. Hydrolysis has been eliminated as a dominant mechanism in the precipitation formation since both the ^{27}Al NMR and Raman investigations reveal that water does not significantly alter the number, or concentration, of the catholyte's chemical species. Three species that were identified include a starting material (Al_2Cl_6), an SO_2 adduct **1**, and a rearranged oxo-like species with a $SOCl_2$ moiety. Scheme 1 shows some of the potential pathways to these species. Both time and temperature control the kinetics of this complex reaction system. However, over time a precipitate will form that appears to be in equilibrium with the mother liquor. Therefore, based on these data, low-temperature storage will prevent precipitate formation. Nevertheless, even after prolonged high-temperature storage, the catholyte is expected to remain active due to the interaction of the solution, precipitate, and the relative amounts of unreacted species remaining. Hence, the reserve battery is expected to function normally, although formation of excessive amounts of precipitate may impair the mechanical aspects of the battery activation process. Additional studies on the extent of reactivity that this catholyte can display under more extreme conditions as well as the electrochemical behavior of the stored material remain to be investigated.

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Supporting Information Available: CIF data are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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