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Studies to improve the Li/SO_2Cl_2 cell

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The performance of the Li/SO_2Cl_2 primary cell was studied as a function of the type of the carbon cathode, cathode catalysts and electrolyte additives. Solutions of $LiAlCl_4$ in SO_2 are more conductive than those in SO_2Cl_2 and, consequently, the electrolyte resistance in the Li/SO_2Cl_2 cell decreases during discharge as one mole of SO_2 is formed per mole of SO_2Cl_2. The replacement of the low surface area Chevron acetylene black carbon with the high surface area Ketjenblack carbon cathode increases cell capacity and reduces cathode polarization. The high surface area carbon, however, causes a deterioration in the storability of the cell, manifested as higher self-discharge rate. The use of carefully purified SO_2Cl_2, and of Ca^{2+} as an additive to the electrolyte, has been found to reduce the voltage delay of the cells stored at 70° C. The low temperature discharge capacity of the Li/SO_2Cl_2 cell can be increased with the addition of SO_2. Furthermore, the added SO_2 appeared to improve the storability of the cells. Cathodes doped with a catalyst consisting of a mixture of polyacrylonitrile and Co, Ni or Fe-salts, after heat treatment at 800° C, demonstrated 350–500 mV gain in the load voltage at 25 mA cm^{-2}. Catalysed cells stored at 70° C retained their higher cell voltage but, like the uncatalysed cells, showed a loss in capacity.

1. Introduction

The Li/SO_2Cl_2 primary cell continues to attract research and development interest due to many potential advantages of this cell over the Li/$SOCl_2$ cell [1–3]. These include enhanced safety, higher cell capacity and load voltage. The Li/SO_2Cl_2 cell is believed to be safe because of the absence of sulphur as a discharge product, which is thought to be a participant in the safety hazards of the cell. Absence of sulphur, which has limited solubility in the oxyhalide electrolyte, also implies higher cell capacity for the Li/SO_2Cl_2 cell *vis à vis* the Li/$SOCl_2$ cell since the life of these liquid electrolyte cells is usually determined by the amount of solid discharge product precipitated within the cathode pores. Another advantage of the Li/SO_2Cl_2 cell is its higher open-circuit potential of 3.9 V, which should translate into higher load voltage. Although this expected high load voltage was realized at low rates it did not persist at high discharge rates due to excessive cathode polarization. The Li/SO_2Cl_2 cell reportedly also suffers from considerable self-discharge because of a higher rate of lithium anode corrosion than that experienced by the Li/$SOCl_2$ cell.

Several authors have studied, and suggested solutions to, the various problems of the Li/SO_2Cl_2 cell. For example, Klinedinst and Gary [4] have found that the use of a blend of Chevron acetylene black and a high surface area/high structure carbon such as Ketjenblack reduces cathode polarization. They also indicated that coating the lithium anode with a polymer and using an alternative lithium salt, $LiGaCl_4$, lowered anode corrosion in the cell [4]. Cathode catalysts such as platinum or metallomacrocyclic complexes such as cobalt phthalocyanine (CoPc) were shown by Doddapaneni [5, 6] to significantly improve the rate capability. Liang *et al.* [7], in an attempt to mitigate the self-discharge problem, modified the SO_2Cl_2/$LiAlCl_4$ electrolyte by adding 0.5 M Cl_2. Our own work indicated that Cl_2 addition did not mitigate self-discharge, rather it appeared to exacerbate the problem [3].

Gilman and Wade [8] evaluated the effect of addition of Cl_2 and SO_2 on the discharge of the Li/SO_2Cl_2 cell in which the cathode was fabricated from a United carbon. They found that while Cl_2 reduced polarization at the cathode, SO_2 increased the polarization. However, the latter additive apparently increased the discharge capacity. Many of the issues concerning the Li/SO_2Cl_2 cell remain unsettled, and therefore we have investigated how the cell performance might be improved. Our approach has included the utilization of cosolvents, such as SO_2 and $SOCl_2$, and a catalyst based on a mixture of polyacrylonitrile and a transition metal salt. Klinedinst and Gary [4] have indicated that cosolvents of SO_2 or $SOCl_2$ might be beneficial from anode corrosion point of view. We have reasoned that a SO_2Cl_2/SO_2 binary or a SO_2Cl_2/SO_2/$SOCl_2$ ternary solvent/depolarizer system, instead of SO_2Cl_2 alone, might be desirable for higher electrolyte conductivity, better low temperature discharge performance and lower anode corrosion. An argument in support of the use of SO_2 is that the Li/SO_2-(organic electrolyte) cell has very low self-discharge which is indicative of the formation of a stable lithium interphase in the presence of SO_2 [9]. Also

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the SO_2 cell has good low temperature performance. Yet another advantage of the addition of SO_2 to the electrolyte is that the equilibrium in Equation 1 is shifted to the left, thereby reducing the Cl_2 content which appears to exacerbate lithium anode corrosion.

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2 \qquad (1)$$

To reduce cathode polarization at high discharge rates, we have studied new catalysts derived from the heat-treatment of a mixture of carbon, polyacrylonitrile and a transition metal ion such as Co^{2+}. This catalyst, unlike platinum or metallomacrocyclic complexes, such as cobalt phthalocyanine used previously [1, 5, 6] is inexpensive and readily prepared. We have also investigated inorganic additives to the electrolytes such as alkali and alkaline-earth metal ions to mitigate the voltage delay of the cell.

2. Experimental details

SO_2Cl_2 and $SOCl_2$ (Eastman Kodak) were distilled prior to use. As-received SO_2Cl_2 (or $SOCl_2$) was first refluxed for 30 min with $AlCl_3$. A slight molar excess of dried LiCl was then added to this solution, followed by distilling off SO_2Cl_2 in an argon atmosphere. The distilled SO_2Cl_2 was then refluxed for about 15 h over lithium. The final distillate appeared colourless to faintly greenish-yellow. Gaseous SO_2 (Matheson) was converted to the $LiAlCl_4.xSO_2$ complex ($x \simeq 3$), which is liquid at room temperature, by trapping it over $LiAlCl_4$. In this procedure, SO_2 was passed through a graduated collection tube containing a weighed amount of $LiAlCl_4$ (Anderson Physics) until a requisite amount of SO_2, as determined gravimetrically, was collected. Mixed solvent electrolytes containing SO_2 was prepared by adding a known volume of this complex and then diluting it with SO_2Cl_2 (or $SO_2Cl_2/SOCl_2$) in a volumetric flask. Additional quantities of $LiAlCl_4$, if necessary, was added to obtain the desired molarity of the solute. The ratios of the solvents in the mixed electrolytes are given as molar percentages. The electrolyte preparation was conducted in a drybox under an argon atmosphere.

The conductivity of the various electrolytes was determined using a YSI Model 31 conductivity bridge. The conductivity cell (YSI 3403) containing platinized platinum electrodes was placed in a test tube having the desired electrolyte solution. The cell and the test tube were joined by a Swagelok fitting to make an air-tight seal. The cell constant was determined using standard KCl solution. The conductivity measurements were carried out in a Tenney environmental chamber after equilibrating the cell for one hour at 25, 0 or −30° C. Viscosity measurements on the SO_2Cl_2-based electrolytes were carried out using a size 100 Cannon-Finske routine viscometer. This consisted of measuring the time (efflux time) a given volume of solution takes to flow between two specified marks of the viscometer. The kinematic viscosity in centistokes was then calculated by multiplying the efflux time in seconds by the viscometer constant. The viscometer was positioned in a Neslab constant temperature bath of water-ethylene glycol mixture in such a way as to allow observation of the calibration marks while keeping it constantly submerged in the bath. Efflux time measurements were repeated thrice at each temperature.

Cathode sheets were prepared from Chevron, Ketjenblack (Akzo, EC-700JD), or a blend of these two carbons by mixing with 10 w/o Teflon binder and water, and spreading the mixture on expanded nickel substrate followed by drying. The electrodes were then sintered at 300° C in an inert atmosphere. Cathodes containing the polyacrylonitrile (PAN)-based catalyst were prepared in the following way. Required quantities of PAN (Polysciences, Inc., $M_w = 150\,000$) and cobaltous, iron or nickel-acetate were dissolved in dimethyl formamide (DMF) at around 120° C. Chevron carbon black was added to this solution and was mixed thoroughly. After stripping off DMF by rotary evaporation, the carbon mixture was heat-treated at 800° C for 2–4 h under flowing nitrogen. Cathode sheets were prepared as described above.

Spirally-wound AA-size cells were fabricated in 4.85 cm high cans of 1.32 cm internal diameter (i.d.) and a wall thickness of 0.025 cm. The cell cover contained a glass-to-metal seal, which was fitted with a fill-tube of 0.03 cm i.d. Both the anode and the cathode were 3.6 cm wide; the cathode was about 0.06 cm thick and about 6 cm long. The separator consisted of 0.02 cm thick fiber glass mat obtained from Hollingsworth and Vose. The cell cover was TIG-welded to the can. The can is negative in all cells. Cells were vacuum-filled with the respective electrolytes. Typically the cells contained about 4 ml of the electrolyte and about 0.5 g of carbon and about 0.6 g of lithium. The lithium foil was obtained from Cyprus–Foote Company, PA. These 'short AA' cells were cathode-limited. The cells were discharged galvanostatically at room temperature and −20° C. The currents used were between 1.0 and 0.1 A, which corresponded to a current density between 25 and 2.5 mA cm^{-2}, respectively. The cells were fabricated in a dryroom with less than 2% humidity.

Storage properties of the Li/SO_2Cl_2 cells were evaluated by storing the AA-size cells at 70°C for two weeks and then discharging them at room temperature and −20° C at a series of constant currents between 1.0 and 0.2 A. Voltage delay measurements on the stored cells were carried out by discharging the cells at these currents for five minutes using a fast data acquisition time of 25 ms. A Bascom–Turner Instruments recorder was used for this purpose. Studies with electrolytes containing Ca^{2+}, Na^+, Sr^{2+} and Mg^{2+} were carried out by adding appropriate concentrations of $Ca(AlCl_4)_2$, $NaAlCl_4$, $Sr(AlCl_4)_2$ and $Mg(AlCl_4)_2$ to the SO_2Cl_2–$LiAlCl_4$ (1.5 M) electrolyte. These chloroaluminates were prepared *in situ* in SO_2Cl_2 by reacting $AlCl_3$ with a slight excess of the corresponding metal chloride which had been dried at 150° C under vacuum for four days.

3. Results and discussion

The discharge reaction of the Li/SO_2Cl_2 is well established [1–3] and can be represented by Equation 2 in which one mole of SO_2 is produced per mole of SO_2Cl_2.

$$2Li + SO_2Cl_2 \rightarrow SO_2 + 2LiCl \qquad (2)$$

Both SO_2Cl_2 and SO_2 form complexes with $LiAlCl_4$, which have high ionic conductivities. Thus, a knowledge of the relative conductivities of SO_2Cl_2–$LiAlCl_4$, SO_2–$LiAlCl_4$ and SO_2Cl_2/SO_2–$LiAlCl_4$ solutions is important in gaining a full understanding of the electrochemical behaviour of the Li/SO_2Cl_2 cell. We have found that it is possible to modulate the performance of the Li/SO_2Cl_2 cell, especially its low temperature capacity, with the use of a mixed solvent/depolarizer of $SOCl_2$ and SO_2Cl_2 [10]. In the course of discharge of such a cell the electrolyte is composed of three solvents, namely SO_2Cl_2, $SOCl_2$ and SO_2 whose relative amounts vary with the depth of discharge.

3.1. *Conductivity*

SO_2Cl_2/$LiAlCl_4$-based electrolytes containing various amounts of either SO_2 or $SOCl_2$, or both, were prepared, and their conductivities were measured as a function of temperature. The concentration of $LiAlCl_4$ in these electrolytes was varied between 0.5 and 2.5 M.

The conductivities of four SO_2Cl_2–$LiAlCl_4$ solutions, at 25, 0 and −30° C, are tabulated in Table 1 and graphically presented in Fig. 1. At each temperature, the conductivity increased upon increasing the solute concentration from 0.5 to 1.5 M. For example at 25° C, SO_2Cl_2–$LiAlCl_4$ (0.5 M) showed a conductivity of $2.92 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, while the electrolyte SO_2Cl_2–$LiAlCl_4$ (1.5 M) had a conductivity of $1.03 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. On raising the solute concentration further to 2.5 M, the conductivity either showed a minor increase, or at the lower temperature of −30° C, decreased slightly. It appears that at low temperatures or at high solute concentrations the solution viscosity increases significantly, reducing ionic mobility and, consequently, the conductivity (see below). High $LiAlCl_4$ concentrations can also lead to increases in ion-pairs or large ion-aggregates which reduce ionic conductivity.

Table 1. Conductivities of SO_2Cl_2–$LiAlCl_4$ electrolytes

Solvent	*[$LiAlCl_4$]*/M	*Conductivity*/Ω^{-1} cm^{-1}		
		25° *C*	0° *C*	−30° *C*
SO_2Cl_2	0.5	2.92×10^{-3}	2.73×10^{-3}	2.20×10^{-3}
	1.0	6.98×10^{-3}	5.57×10^{-3}	3.40×10^{-3}
	1.5	1.03×10^{-2}	7.23×10^{-3}	3.64×10^{-3}
	2.5	1.37×10^{-2}	8.72×10^{-2}	3.20×10^{-3}

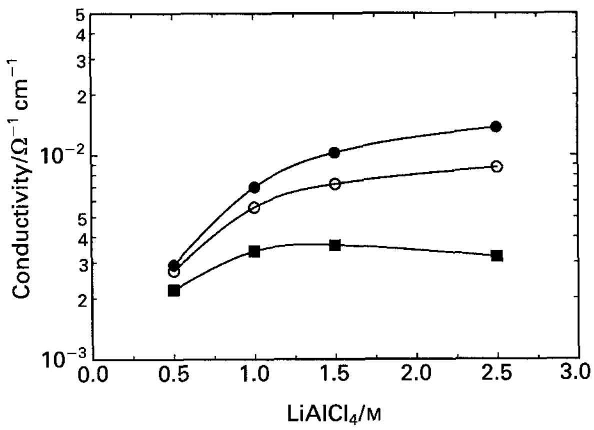


Fig. 1. Conductivities of SO_2Cl_2–$LiAlCl_4$ solutions at three different temperatures: (●) 25° C, (○) 0° C and (■) −30° C.

The conductivities of three SO_2Cl_2/SO_2–$LiAlCl_4$ solutions, each for different concentrations of $LiAlCl_4$, are given in Table 2. The $SO_2Cl_2 : SO_2$ ratios for these electrolytes were 93 : 7, 80 : 20 and 73 : 27 in mol %. The data in Table 2 reveal that as the SO_2 content increases the conductivity of the SO_2Cl_2/SO_2–$LiAlCl_4$ mixed electrolyte at 25° C increases. Generally, the conductivities of the SO_2Cl_2/SO_2–$LiAlCl_4$ electrolytes were higher than those of the solutions without SO_2 for all $LiAlCl_4$ concentrations. For example, the 73/27SO_2Cl_2/SO_2–$LiAlCl_4$ (1.0 M) electrolyte showed a conductivity which is more than twice that of the SO_2Cl_2–$LiAlCl_4$ (1.0 M) electrolyte.

The conductivities of the $SO_2Cl_2/SOCl_2$–$LiAlCl_4$ mixed electrolytes were intermediate between those of the higher conductive $SOCl_2$–$LiAlCl_4$ and the lower conductive SO_2Cl_2–$LiAlCl_4$ solutions (Table 3). Among the three $SO_2Cl_2/SOCl_2/SO_2$–$LiAlCl_4$ ternary electrolytes we have studied, Table 4, that having the composition 68/21/11 $SO_2Cl_2/SOCl_2$/SO_2–$LiAlCl_4$ showed the highest conductivity.

The higher conductivity of the binary and the ternary electrolytes compared to that of the pure

Table 2. Conductivities of SO_2Cl_2/SO_2-based electrolytes

Solvent	*[$LiAlCl_4$]* /M	*Conductivity*/Ω^{-1} cm^{-1}		
		25° *C*	0° *C*	−30 ° *C*
93/7*	0.65	4.59×10^{-3}	4.39×10^{-3}	3.19×10^{-3}
SO_2Cl_2/SO_2	1.0	8.90×10^{-3}	7.08×10^{-3}	4.34×10^{-3}
	1.5	1.17×10^{-2}	8.57×10^{-3}	4.16×10^{-3}
	2.5	1.78×10^{-2}	1.02×10^{-2}	3.20×10^{-3}
80/20	0.50	5.48×10^{-3}	4.50×10^{-3}	3.50×10^{-3}
SO_2Cl_2/SO_2	1.0	1.02×10^{-2}	8.89×10^{-3}	5.41×10^{-3}
	1.5	1.60×10^{-2}	1.20×10^{-2}	5.91×10^{-3}
	2.5	2.20×10^{-2}	1.37×10^{-2}	4.68×10^{-3}
73/27	0.50	6.50×10^{-3}	5.50×10^{-3}	4.02×10^{-3}
SO_2Cl_2/SO_2	1.29	1.88×10^{-2}	1.39×10^{-2}	7.62×10^{-3}
	2.00	2.52×10^{-2}	1.75×10^{-2}	7.80×10^{-3}
	2.50	2.82×10^{-2}	1.78×10^{-2}	6.10×10^{-3}

* Mole ratio

Table 3. Conductivities of $SO_2Cl_2/SOCl_2$ and $SOCl_2$-based electrolytes

Solvent	[*LiAlCl*$_4$] /M	*Conductivity*/Ω^{-1} cm^{-1}		
		25° *C*	0° *C*	−30° *C*
$SOCl_2$	0.5	6.19×10^{-3}	6.10×10^{-3}	4.99×10^{-3}
	1.0	1.32×10^{-2}	1.12×10^{-2}	8.00×10^{-3}
	1.5	1.60×10^{-2}	1.33×10^{-2}	8.42×10^{-3}
	2.5	1.75×10^{-2}	1.20×10^{-2}	5.73×10^{-3}
78/22	0.5	3.75×10^{-3}	3.65×10^{-3}	3.00×10^{-3}
$SO_2Cl_2/SOCl_2$	1.0	8.03×10^{-3}	7.00×10^{-3}	4.35×10^{-3}
	1.5	1.40×10^{-2}	1.00×10^{-2}	6.00×10^{-3}
	2.5	1.60×10^{-2}	9.81×10^{-3}	4.00×10^{-3}
47/53	0.5	4.81×10^{-3}	4.20×10^{-3}	3.70×10^{-3}
$SO_2Cl_2/SOCl_2$	1.0	1.02×10^{-2}	8.22×10^{-3}	5.51×10^{-3}
	1.4	1.30×10^{-2}	1.05×10^{-2}	5.80×10^{-3}
	1.8	1.50×10^{-2}	1.10×10^{-2}	5.00×10^{-3}

SO_2Cl_2 electrolyte can be explained in terms of the higher dielectric constant of SO_2 and the lower viscosities of SO_2 and $SOCl_2$. The dielectric constants for SO_2, $SOCl_2$ and SO_2Cl_2 are 12 (at 0° C), 9.25 (20° C) and 9.15 (22° C), respectively. Therefore, from purely electrostatic point of view SO_2 is expected to yield a higher conductive solution than SO_2Cl_2 by providing a stronger ionizing medium. Similarly, SO_2 has a viscosity of 0.21 centistokes, which is considerably lower than the viscosities of $SOCl_2$ and SO_2Cl_2 which are 0.37 and 0.41 centistokes, respectively. The effect of this low viscosity is also reflected in the higher conductivity of the pure $SO_2.xLiAlCl_4$ complex, which at room temperature is about $10^{-1}\,\Omega^{-1}\,cm^{-1}$ for $x \simeq 3$.

The viscosity data in Table 5, for several of the electrolytes in the temperature range between −20 and 20° C, reveal some predictable trends. A decrease in the temperature increases the viscosity. Similarly, an increase in the solute concentration also increases the viscosity as borne out by the data for the SO_2Cl_2−$LiAlCl_4$ solutions having solute concentrations of 1.5 and 2.5 M. The viscosities of the mixed electrolytes, 80/20 SO_2Cl_2/SO_2−$LiAlCl_4$ (1.5 M) and 66/17/17 $SO_2Cl_2/SO_2/SOCl_2$−$LiAlCl_4$ (1.5 M), were found to be lower than that of the SO_2Cl_2−$LiAlCl_4$ (1.5 M) solution at all temperatures. Below 0° C, the viscosity of the ternary solvent-based electrolyte 66/17/17 $SO_2Cl_2/SO_2/SOCl_2$−$LiAlCl_4$ (1.5 M) was lower than that of all the other electrolytes.

Table 4. Conductivities of $SO_2Cl_2/SOCl_2/SO_2$−$LiAlCl_4$ ternary electrolytes

Solvent	[*LiAlCl*$_4$] /M	*Conductivity*/Ω^{-1} cm^{-1}		
		25° *C*	0° *C*	−30° *C*
68/21/11	0.50	5.26×10^{-3}	4.65×10^{-3}	3.57×10^{-3}
$SO_2Cl_2/SO_2/SOCl_2$	1.0	1.34×10^{-2}	1.11×10^{-2}	6.47×10^{-3}
	1.5	1.80×10^{-2}	1.43×10^{-2}	7.15×10^{-3}
	2.5	2.52×10^{-2}	1.53×10^{-2}	5.46×10^{-3}
66/17/17	0.68	6.50×10^{-3}	5.87×10^{-3}	4.14×10^{-3}
$SO_2Cl_2/SO_2/SOCl_2$	1.0	1.10×10^{-2}	9.23×10^{-3}	5.65×10^{-3}
	1.5	1.64×10^{-2}	1.20×10^{-2}	6.27×10^{-3}
	2.5	2.10×10^{-2}	1.40×10^{-2}	5.42×10^{-3}
77/11/12	0.5	4.27×10^{-3}	3.84×10^{-3}	2.82×10^{-3}
$SO_2Cl_2/SO_2/SOCl_2$	1.0	9.78×10^{-3}	8.00×10^{-3}	4.57×10^{-3}
	1.5	1.37×10^{-2}	1.01×10^{-2}	4.92×10^{-3}
	2.5	1.60×10^{-2}	1.07×10^{-2}	3.63×10^{-3}

Table 5. Viscosity of some SO_2Cl_2-based electrolytes

Electrolyte	*Viscosity*/centistokes				
	−20°*C*	−10°*C*	0°*C*	10° *C*	20° *C*
SO_2Cl_2−$LiAlCl_4$ (1.5 M)	3.971	2.822	2.102	1.662	1.368
SO_2Cl_2−$LiAlCl_4$ (2.5 M)	8.443	5.437	3.837	2.810	2.163
80/20 SO_2Cl_2/SO_2−$LiAlCl_4$ (1.5 M)	3.030	2.126	1.625	1.320	1.087
66/17/17 $SO_2Cl_2/SO_2/$ $SOCl_2$−$LiAlCl_4$ (1.5 M)	2.675	2.102	1.637	1.320	1.124

The ability of sulphur oxychlorides and SO_2 to form complexes with $LiAlCl_4$ is well known [4, 12]. For example, the complexes $Li^+(SOCl_2)_2AlCl_4^-$ and $Li^+(SO_2)_3AlCl_4^-$ are believed to exist, respectively, in solutions of $LiAlCl_4$ in $SOCl_2$ and SO_2. By analogy we may conclude that complexes such as $Li^+(SO_2Cl_2)_2AlCl_4^-$, $Li^+(SOCl_2)(SO_2Cl_2)AlCl_4^-$ and $Li^+(SO_2Cl_2)(SO_2)AlCl_4^-$ probably exist in SO_2Cl_2−$LiAlCl_4$, $SO_2Cl_2/SOCl_2$−$LiAlCl_4$ and SO_2Cl_2/SO_2−$LiAlCl_4$ solutions, respectively. At normal temperature and pressure, the equilibrium constant for the dissociation reaction in Equation (1) is 0.01 [13]. This implies that SO_2Cl_2 normally contains about 0.35 molar SO_2 and 0.35 molar Cl_2. In the 93/7 SO_2Cl_2/SO_2 mixed solvent electrolyte, the amount of SO_2 added is equivalent to about 2.5 M which would shift the equilibrium (see Equation 1) significantly to the left with a substantial amount of SO_2 still present to form complexes of the type mentioned above. The Cl_2 present in such solutions should be very small and that should reduce the corrosion of the lithium anode.

3.2. *Discharge*

The discharge performance of the Li/SO_2Cl_2 cell was evaluated as a function of the nature of the carbon cathode, type of electrolyte, discharge current and temperature. Hermetically sealed, AA-size cells were employed as the test vehicle for these studies.

The discharge behaviour of the Li/SO_2Cl_2 and Li/$SOCl_2$ cells are compared in Fig. 2. The Li/SO_2Cl_2 cell delivered about 20% higher capacity than the Li/$SOCl_2$ cell when discharged at 5 mA cm^{-2}. The reason for this difference is that the Li/$SOCl_2$ cell, unlike its SO_2Cl_2 counterpart, produces sulphur as a discharge product (Equation 3) which due to its limited solubility precipitates out within the cathode pores. This shortens the cell life because the sulphur takes up a fraction of the pores which otherwise would be available for LiCl deposition. The reaction is:

$$4Li + 2SOCl_2 \rightarrow S + SO_2 + 4LiCl \qquad (3)$$

Besides the absence of sulphur, the discharge of the Li/SO_2Cl_2 cell, according to Equation 2, yields one

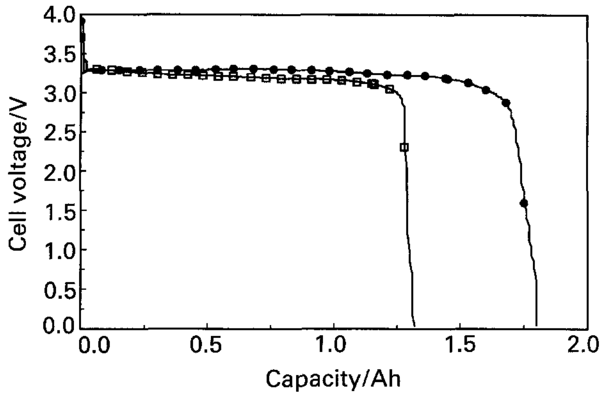


Fig. 2. Typical discharge curves of Li/SO_2Cl_2 (●) and Li/$SOCl_2$ (□) AA-cells at room temperature; current: 0.2 A ($\simeq$ 5 mA cm^{-2}).

mole of SO_2 per each mole of SO_2Cl_2. Since the SO_2Cl_2/SO_2–$LiAlCl_4$ solutions have higher conductivity than the SO_2Cl_2–$LiAlCl_4$ solution, the electrolyte conductivity increases as the discharge proceeds. From the specifications of our AA-size cell and a discharge capacity of 1.3 Ah, we calculate that the composition of the electrolyte at the end of discharge becomes 50/50 SO_2Cl_2/SO_2–$LiAlCl_4$ (~ 1.7 M). At this point the conductivity of the electrolyte increases from an initial value of $7 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ to about $3 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$. If electrolyte conductivity were the sole contributor to cell resistance, this would lower the cell resistance, and even lead to a small rise in the load voltage of the cell, as discharge proceeds. We may not, however, see this rise in electrolyte conductivity reflected as higher load voltage since the end-of-discharge of the cell is signalled by the voltage polarization associated with the choking of the carbon cathode by LiCl. The higher conductivity of the SO_2Cl_2/SO_2 solutions also explains the high rate capability of the SO_2Cl_2 cell. A Li/$SOCl_2$ cell, on the other hand, produces only half a mole of SO_2 for each mole of $SOCl_2$, and the relative increase in the electrolyte conductivity during discharge of this cell is less. Figure 2 shows that the Li/SO_2Cl_2 cell has a slightly higher load voltage than the Li/$SOCl_2$ cell.

Three different cathodes, based on Chevron acetylene black, Ketjenblack and a 75 w/o : 25 w/o blend of Chevron/Ketjenblack, were used to evaluate the effect of the nature of the carbon cathode on the discharge capacity of the Li/SO_2Cl_2 cell. The surface area of the finished cathodes were measured to be 40, 880 and 194 $m^2\,g^{-1}$, respectively (Table 6). The capacities delivered by the AA-size cells depended on the type of the carbon electrode and were between 1.2 and 1.8 Ah for discharge currents between 1.0 and 0.1 A. The dependence of capacity on the discharge current is shown in Fig. 3 for cells containing the Chevron cathode. Typical discharge performances of the three types of carbon cathodes are illustrated in Fig. 4 for cells containing the SO_2Cl_2–$LiAlCl_4$ (1.5 M) electrolyte. (The capacities are normalized with respect to the cathode volume). The correlation of cell capacity to cathode surface area, presented in Table 6, indicates that the larger the surface area, the higher is the capacity and load voltage. This is further evidenced in Fig. 5 which shows the average cathode utilization normalized with respect to its weight (Ah g^{-1}) and volume (Ah cm^{-3}). The data reflect the expected trend of higher capacity for a cathode having a higher surface area, since a larger surface area cathode with its higher porosity can achieve higher capacity and load voltage, respectively, by accommodating more LiCl and by lowering the effective current density per carbon mass. Our results do not agree with those of Klinedinst and Gary [4], who observed an unusual maximum in the delivered capacity for the 75 w/o Chevron : 25 w/o Ketjenblack carbon blend.

Table 6. Capacity and load voltage of AA-size Li/SO_2Cl_2 cells using different carbon cathodes at 1.0 *A and room temperature. Electrolyte =* SO_2Cl_2–$LiAlCl_4$ (1.5 M)

Cathode	*Surface Area** /$m^2\,g^{-1}$	*Average capacity* /Ah	*Average load voltage* /V
Chevron	40	1.2	3.1
75/25 Chevron/Ketjenblack	194	1.5	3.4
Ketjenblack	880	1.8	3.5

* Measured by the BET method

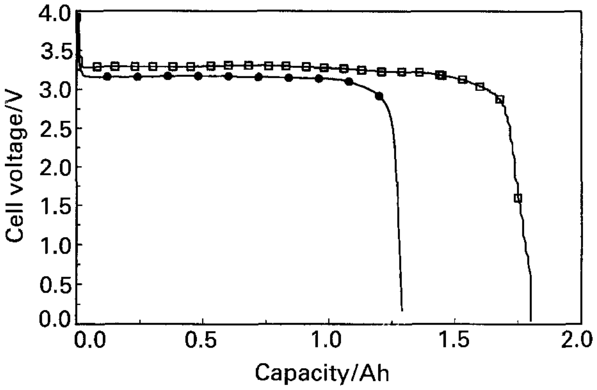


Fig. 3. Typical discharge curves for AA-size Li/SO_2Cl_2 cells, using Chevron carbon cathodes, at room temperature and two different currents: (●) 15 mA cm^{-2}; (□) 5 mA cm^{-2}.

The relative performance of the three carbon cathodes at the lower temperature of −20° C was similar to that at room temperature (Fig. 6). Again,

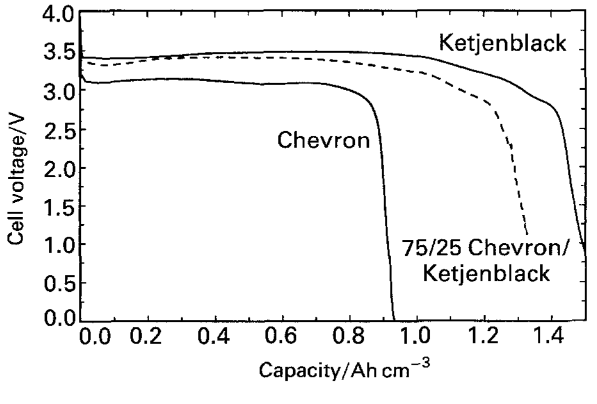


Fig. 4. Typical discharge curves for AA-size Li/SO_2Cl_2 cells containing the three different types of carbon cathodes at room temperature. Current: 1.0 A.

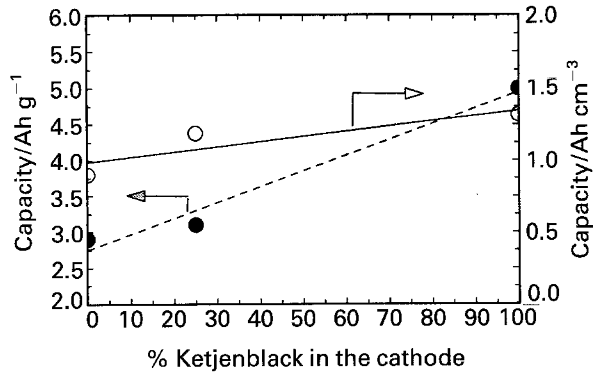


Fig. 5. Correlation between the cell capacity and the weight and volume of the carbon cathode. Electrolyte was SO_2Cl_2–$LiAlCl_4$ (1.5 M). The discharge was at 1.0 A.

the cell with Ketjenblack carbon showed the highest capacity along with a load voltage which was ~ 500 mV higher than that of the cell containing the Chevron carbon.

3.3. *Performance of different electrolytes*

At room temperature, all three carbon cathodes displayed similar discharge capacities with the SO_2Cl_2, SO_2Cl_2/SO_2 and the $SO_2Cl_2/SO_2/SOCl_2$-based electrolytes. However, the use of the mixed electrolytes, especially those containing the SO_2Cl_2/SO_2 binary mixture, led to higher capacities and load voltages at −20° C. This is evident in Fig. 7 which compares the discharge data of cells containing Chevron cathode and the electrolytes SO_2Cl_2–$LiAlCl_4$ (1.5 M), 90/10 SO_2Cl_2/SO_2–$LiAlCl_4$ (1.5 M) and the 80/20 SO_2Cl_2/SO_2–$LiAlCl_4$ (1.5 M), at −20° C and 1.0 A. The use of the SO_2/SO_2Cl_2-based binary electrolytes resulted in about 0.2 V higher load voltage and approximately 0.1 Ah/cm^3 higher capacity. It may be argued that the removal of a substantial amount of Cl_2 by the addition of SO_2 improves the kinetics of crystallization of LiCl produced during discharge at −20° C. The solubility of LiCl in SO_2Cl_2 is less than 10^{-6} mol dm^{-3}; consequently, practically all of the LiCl produced will precipitate in the porous carbon cathode. What it implies is that the cell capacity would be affected by the manner in which the LiCl is accommodated in the cathode. It is possible that when a sufficient amount of SO_2 is initially present, it influences the nucleation of LiCl more favourably than when it is introduced during the course of discharge. Thus, the increased voltage and capacity of SO_2-containing cells may be ascribed to the beneficial effect of the initial morphology of the LiCl formed in the cathode. Interestingly, this difference in the −20° C performance vanished when the current was less than 2 mA cm^{-2}.

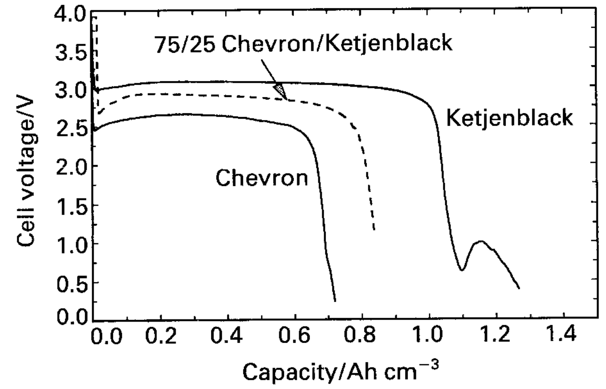


Fig. 6. Typical discharge curves for AA-size Li/SO_2Cl_2 cells containing the three types of carbon cathodes at −20° C and 1.0 A.

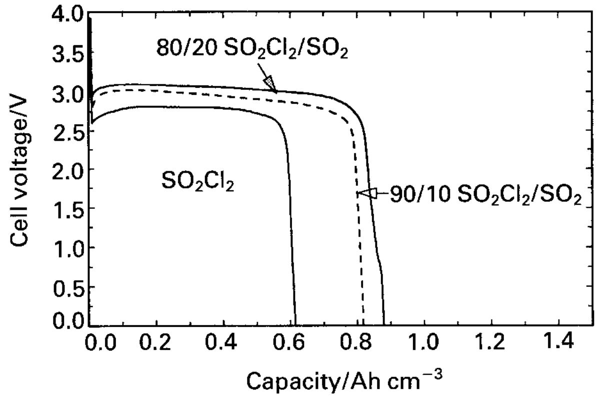


Fig. 7. Comparison of the discharge behaviour of cells containing the 90/10 SO_2Cl_2/SO_2–$LiAlCl_4$ (1.5 M) and the 80/20 SO_2Cl_2/SO_2–$LiAlCl_4$ (1.5 M) mixed electrolytes to that of the cell containing the SO_2Cl_2–$LiAlCl_4$ (1.5 M) electrolyte at −20° C and 1.0 A. Cathode was based on Chevron carbon.

3.4. *Storage properties*

The storage properties of the Li/SO_2Cl_2 cells, i.e. voltage delay and capacity retention, were studied after storing the cells at 70° C for two weeks and discharging them either at room temperature or −20° C. Discharge currents between 1.0 and 0.2 A were used. The storability of the cells was evaluated as a function of different electrolyte compositions and cathode types. In general, all the stored cells showed losses in capacity and load voltage, the extent of which primarily depended on the type of carbon cathode employed.

Voltage delay is defined as the time the voltage of cell, upon its startup, remains below the operationally acceptable limit of 2.0 V. Previous studies [13] have shown voltage delays of the order of minutes when cells were discharged at ~ 20 mA cm^{-2} after storage for two weeks at 70° C. Voltage delay measurements we have carried out on stored Li/SO_2Cl_2 cells, however, showed better performance. For example, cells containing Chevron cathodes discharged at 1.0 A (~ 25 mA cm^{-2}) after storage at 70° C for two weeks showed a voltage delay of only 4 s. This improved voltage delay behaviour was probably the result of the carefully purified SO_2Cl_2-based electrolytes we used. This is exemplified by the data in Fig. 8 which compares the voltage delay characteristics of cells containing electrolytes in purified and as-received SO_2Cl_2. The voltage delay was reduced by half with the purified electrolyte.

The data presented in Fig. 9 for two sets of cells containing Chevron cathodes, one discharged at

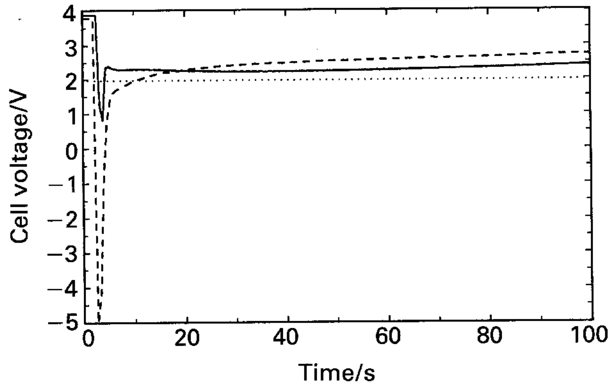


Fig. 8. Comparison of the voltage delay behaviour of cells containing electrolytes prepared with purified (———) and as-received (– – –) SO_2Cl_2. The cells were discharged at room temperature after storage at 70° C for two weeks. Current: 1.0 A.

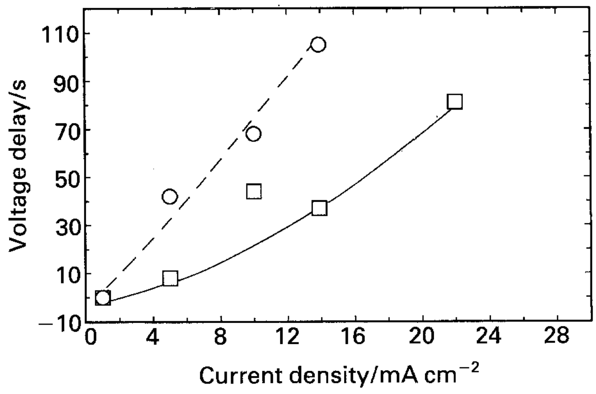


Fig. 10. Voltage delay behaviour of Li/SO_2Cl_2 cells discharged at room temperature (———) and −20° C (– – –), as a function of current density. The cathode was based on 75/25 Chevron/Ketjenblack carbon and the electrolyte was SO_2Cl_2–$LiAlCl_4$ (1.5 M).

room temperature and the other discharged at −20° C, illustrate the threshold current density above which stored Li/SO_2Cl_2 cells exhibited voltage delay. For currents $\leq 10\,mA\,cm^{-2}$ the cells did not show any voltage delay at room temperature. However, at −20° C a voltage delay of 10 s was observed for $10\,mA\,cm^{-2}$. It should be pointed out here that the voltage delay was very similar for the different electrolytes and no advantage was obtained by using mixed electrolytes.

The voltage delay of cells containing the 75/25 Chevron/Ketjenblack carbon cathodes was significantly longer than that of cells with the Chevron cathodes. The relevant data for these cells are presented in Fig. 10. At room temperature, the cells showed a voltage delay of approximately 10 s already at $5\,mA\,cm^{-2}$, while at −20° C a voltage delay of about 40 s was observed at about $5\,mA\,cm^{-2}$.

In fact, among the different cathodes those containing the highest surface area Ketjenblack carbon led to the longest voltage delay. This is clearly evident in Fig. 11 which compares the voltage delay observed at room temperature of cells using the Chevron, Ketjenblack and the 75/25 Chevron/Ketjenblack carbon cathodes at 1.0 A. Our observation is similar to the findings of Klinedinst and Gary [4]. They attributed this to leaching into the electrolyte of species from the cathode that adversely affect the anode surface properties. An alternative explanation we propose here is that the high surface area carbon promotes the dissociation of SO_2Cl_2 (Equation 1) to form excessive amounts of Cl_2 which in turn extensively corrodes and passivates the lithium anode as shown in Equation 4:

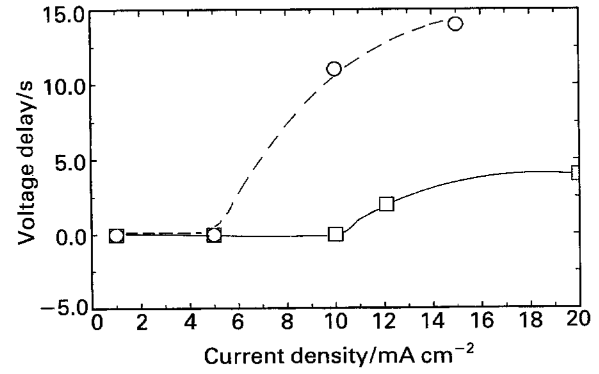


Fig. 9. Voltage delay behaviour of Li/SO_2Cl_2 cells discharged at room temperature (——) and −20° C (– – –), as a function of current density. The cathode was based on Chevron carbon and the electrolyte was SO_2Cl_2–$LiAlCl_4$ (1.5 M).

$$2Li + 2Cl_2 \rightarrow 2LiCl \qquad (4)$$

Since LiCl is insoluble in SO_2Cl_2, continued corrosion of the lithium anode during cell storage would require a mechanism by which the LiCl film can be dissolved and reprecipitated. On the one hand, this can occur via the reactions shown in Equations 5 and 6, borrowed from the mechanism proposed to explain the voltage delay behaviour of $Li/SOCl_2$ cells [14]. In this mechanism the Lewis base LiCl is made soluble by the Lewis acid $AlCl_3$ and the dissolved LiCl film is reprecipitated at another location on the lithium anode.

$$nSO_2Cl_2.LiAlCl_4 \rightleftharpoons LiCl + AlCl_3.nSO_2Cl_2 \qquad (5)$$

$$AlCl_3.nSO_2Cl_2 + LiCl_{(film)} \rightleftharpoons LiAlCl_4.nSO_2Cl_2 \qquad (6)$$

Alternatively, it is also possible to visualize a Cl_2-assisted LiCl film growth mechanism in which the Cl_2 would exchange with LiCl as shown in Equation 7 and help dissolve it in one location and deposit at another, thereby promoting the continued corrosion of the lithium anode in a dissolution/deposition

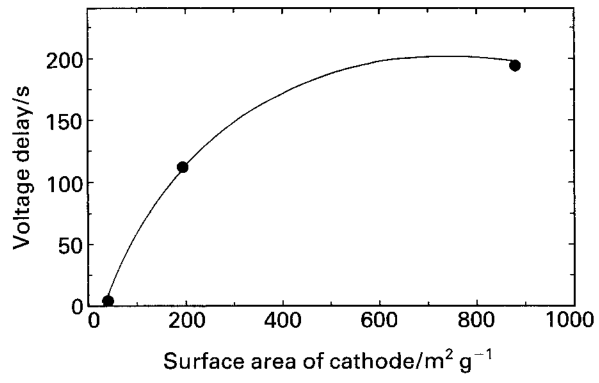


Fig. 11. Comparison of the voltage delay and surface area of the different cathodes used in Li/SO_2Cl_2 cells.

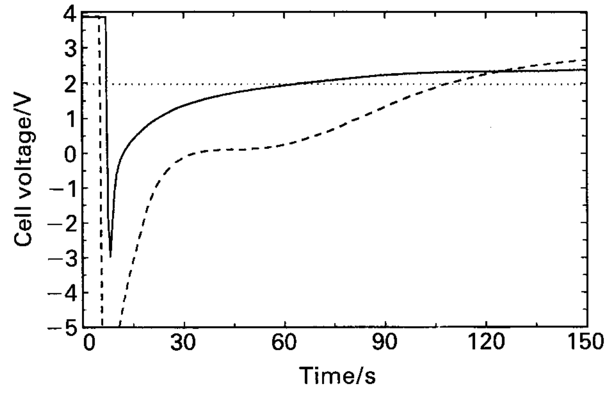


Fig. 12. Comparison of the voltage delay of cells with (———) and without (— — —) Ca^{2+} as the electrolyte additive. Cathode was 75/25 Chevron/Ketjenblack. The discharge was performed at 1.0 A at room temperature.

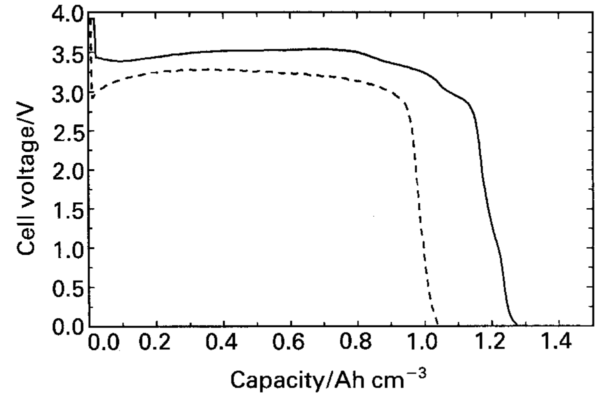


Fig. 14. Storage behaviour of Li/SO$_2$Cl$_2$ cells using 75/25 Chevron/Ketjenblack cathodes. Electrolyte used was SO$_2$Cl$_2$–LiAlCl$_4$ (1.5 M). Discharge current: 1.0 A at room temperature. (— — —) Stored cell; (———) fresh cell.

process.

$$2LiCl^* + Cl_2 \rightleftharpoons 2LiCl + Cl_2^* \quad (7)$$

With a view to minimizing the voltage delay of Li/SO$_2$Cl$_2$ cells, we have investigated electrolyte additives such as Na$^+$, Ca^{2+}, Sr^{2+} and Mg^{2+}. The rationale is that these ions of metals less electropositive than lithium will plate on the lithium anode surface, and will change the composition of the solid electrolyte interphase to afford better corrosion protection without affecting Li$^+$ transport through the interphase. The cell will in turn show reduced voltage delay.

Among the various additives, Ca^{2+} appeared to reduce voltage delay considerably, especially in cells using the high surface area cathodes. This is shown in Fig. 12 which compares the data for cells containing the 75/25 Chevron/Ketjenblack cathodes. Addition of 2 mM of Ca^{2+}, as Ca(AlCl$_4$)$_2$, to the electrolyte lowered the voltage delay from 115 s to 67 s. The magnitude of the overall voltage depression was also lower. Increasing the concentration of Ca^{2+} to 10 or 50 mM did not bring about any noticeable improvement. Also, the effect of adding the ions Na$^+$, Sr^{2+} and Mg^{2+} to the cell electrolyte was insignificant.

The discharge capacity and voltage of stored (two weeks at 70° C) Li/SO$_2$Cl$_2$ cells are compared to those of fresh cells in Figs 13–15. Cells containing Chevron cathodes showed better storability than those containing the other two types of cathodes. Those with Ketjenblack cathodes lost about 30% of the capacity and about 350 mV of the load voltage after the storage (Fig. 15). The corresponding decreases in the capacity and load voltage for the Chevron cells were about 15% and about 100 mV (Fig. 13). The mixed cathode cells lost about the same amount of capacity (Fig. 14) as the Chevron cells.

It is interesting to note here that stored cells containing the Chevron cathodes and the SO$_2$Cl$_2$/SO$_2$ mixed electrolytes showed lower capacity loss than those with the baseline SO$_2$Cl$_2$–LiAlCl$_4$ (1.5 M) electrolyte which did not contain SO$_2$. However, this improvement in storability was not observed either with cells utilizing the Ketjenblack and the 75/25 Chevron/Ketjenblack cathodes or with the 66/17/17 SO$_2$Cl$_2$/SO$_2$/SOCl$_2$–LiAlCl$_4$ (1.5 M) ternary electrolyte. A possible explanation for this is that the amount of Cl$_2$ produced from SO$_2$Cl$_2$ dissociation is probably the least in cells containing the Chevron carbon, and the addition of SO$_2$ shifts equilibrium (Equation 1) substantially to the side of SO$_2$Cl$_2$ so that corrosion

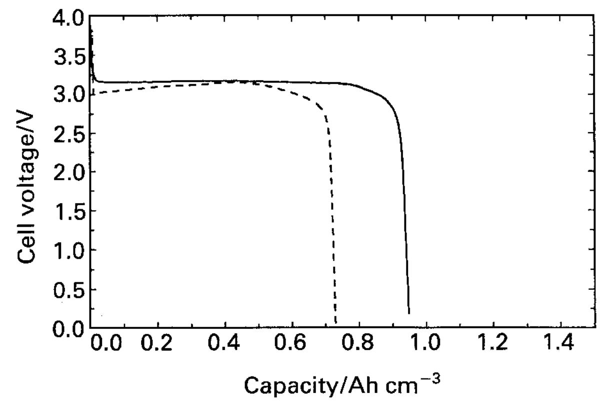


Fig. 13. Storage behaviour of Li/SO$_2$Cl$_2$ cells with Chevron cathodes. The electrolyte was SO$_2$Cl$_2$–LiAlCl$_4$ (1.5 M). The current was 1.0 A and the discharge was at room temperature. (— — —) Stored cell; (———) fresh cell.

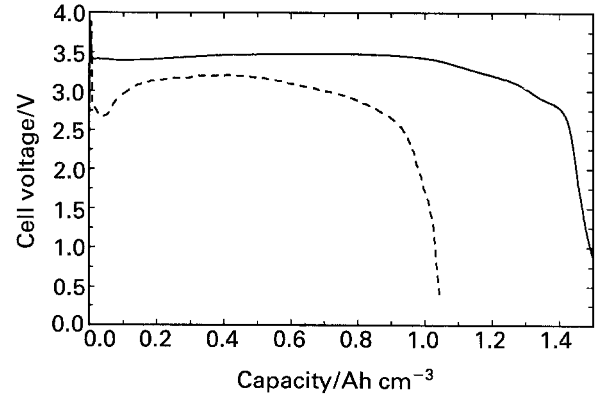


Fig. 15. Storage behaviour of Li/SO$_2$Cl$_2$ cells using Ketjenblack cathodes. Electrolyte used was SO$_2$Cl$_2$–LiAlCl$_4$ (1.5 M). The cell was discharged at 1.0 A at room temperature. (— — —) Stored cell; (———) fresh cell.

reactions of the types illustrated in Equations 4–7 are probably suppressed considerably.

3.5. *Catalyst*

To find an inexpensive and effective remedy to the cathode polarization of the Li/SO_2Cl_2 cell at very high rates, especially on low surface area carbons like the Chevron acetylene black, we have investigated a new type of catalyst based on polyacrylonitrile and a transition metal salt. The catalyst was formed *in situ* on Chevron acetylene black carbon. Before being converted into electrodes, the carbon was mixed with a mixture of polyacrylonitrile, $-\!(CH_2{-}CH(CN))\!-_n$, and cobalt, nickel or iron acetate and heated at 800° C in an inert atmosphere for about 4 h. Control experiments indicated that neither PAN nor the metal salt alone catalysed the reduction of SO_2Cl_2. It should be noted that this catalyst was previously identified as a promising system for the reduction of oxygen, in both acidic and alkaline aqueous electrolytes [15].

The load voltage at 25 mA cm^{-2} of a catalysed cell containing Chevron cathode doped with a mixture of 10 wt % PAN and 2 wt % Co was 3.5 V while that of the uncatalysed cell was 3.1 V, a gain of 400 mV in the catalysed cell (Fig. 16). The discharge capacities of the uncatalysed and the catalysed cells were identical. Chevron cathodes containing either 10 w/o PAN or 2 w/o Co alone behaved either similar to or worse than the uncatalysed cathodes. When the composition of the cathode catalyst was changed to 5 w/o PAN and 2 w/o Co, a slightly inferior catalytic activity was observed. Also, the cathode containing 20 w/o PAN and 2 w/o Co yielded significantly lower capacity than that obtained with the other two catalyst compositions.

When the transition metal was changed to iron or nickel, catalytic activity similar to or better than that achieved with cobalt was realized. An increase of over 0.5 V in the load voltage was obtained with the nickel catalyst while the increase with iron catalyst was ~ 0.4 V. The voltage of the cell containing the iron catalyst, however, showed an initial depression, and this we attribute to the solubility of the catalyst in the electrolyte. The dissolved catalyst apparently increased the voltage delay of the cell by reacting with the lithium anode.

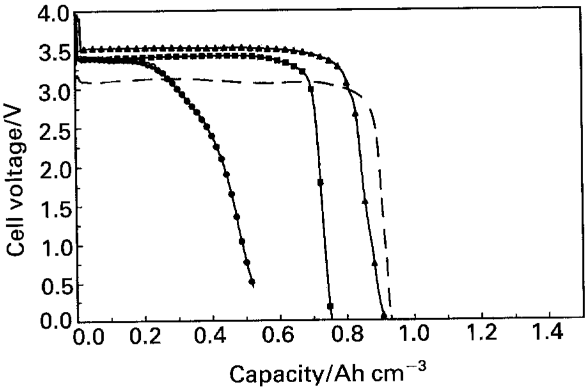


Fig. 16. Discharge capacity of catalysed cells having different cathode compositions. (■) 5 w/o PAN + 2 w/o Co; (▲) 10 w/o PAN + 2 w/o Co; (●) 20 w/o PAN + 2 w/o Co. Current: 1.0 A. The discharge was at room temperature. The discharge plot of an uncatalysed cell (— — —) is also shown for comparison.

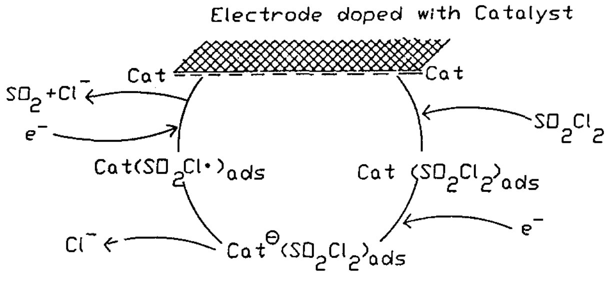
The catalysed cells were also examined for their storability at 70° C. In general, they showed voltage delay and capacity loss very similar to that of uncatalysed cells. Nevertheless, all the cathodes demonstrated excellent catalytic activity even after prolonged storage at 70° C. We conclude that except for the iron system, the catalysts had no effect on the voltage delay or storage behaviour of the Li/SO_2Cl_2 cells.

The catalytic activity of the PAN/transition metal catalysts as well as the storability of the Li/SO_2Cl_2 cells containing them compares very well with those of the metallomacrocyclic catalysts such as CoPc or CoTAA (cobalt tetraazaannulene). While the PAN-containing catalysts are prepared from inexpensive materials *in situ* via a simple procedure, the synthesis of CoPC or CoTAA is tedious, and they are costly. Our data clearly show that the PAN-based catalysts are effective alternatives to the costly catalysts based on noble metals or metallomacrocyclic complexes.

The specie(s) which gives rise to the activity of the PAN-based catalysts has not yet been fully identified. However, some preliminary data we have obtained are worth mentioning. The gases collected from the thermal treatment of a carbon/PAN/cobaltous acetate mixture at 800° C primarily consisted of NH_3. X-ray analysis of the residues remaining after the thermolysis indicated the presence of elemental cobalt along with carbon. Similar results were also observed with the carbon/PAN/nickel acetate mixture; finely divided nickel metal was formed in the carbon matrix as a result of the thermolysis at 800° C. The NH_3 certainly comes from the PAN and the elimination of it as depicted in Equation 6 will leave a residue of carbon.

$$-\!(CH_2{-}CH(CN))\!-_n \rightarrow n\mathrm{NH_3} + 3n\mathrm{C} \qquad (8)$$

Indeed, PAN is a well known precursor for the preparation of a variety of carbon fibres [16]. Whether or not a complete elimination of the nitrogen from PAN occurs at 800° C is not known at this time although an i.r. spectrum of the residue from the pyrolysis indicated absence of CN groups. The PAN may have a dual role in the catalysis. First, it may serve as a reducing agent to convert the metal ion into elemental form; and, second, the carbon produced from pyrolysis of PAN may serve as a binding agent to attach the metal to the carbon electrode matrix. The reducing agent in this scheme may be the NH_3. When PAN and a metal salt are dissolved in dimethyl formamide the metal ion probably complexes with PAN via the lone pair electrons on the CN group on removal of the solvent. The resulting PAN-metal salt complex apparently has the ideal structural disposition to enable the reduction of the metal ion to the elemental



Scheme I. Schematic representation of the mechanism of electrocatalytic reduction of SO_2Cl_2.

form upon pyrolysis and to bind the metal to the cathode matrix. In a recent study we have identified finely divided metal (Co or Ni) also in carbons doped with cobalt or nickel phthalocyanine after thermolysis at 800° C [17]. This suggests that the active catalysts derived from the metallomacrocycles and the PAN/metal salts are probably the same. Surface areas of the catalyzed ($44\,m^2\,g^{-1}$) and uncatalysed ($40\,m^2\,g^{-1}$) Chevron carbons were not significantly different. Whatever the active catalyst specie is, the regenerative cycle schematically shown in Scheme 1 can explain the catalysed reduction of SO_2Cl_2. This mechanism is essentially similar to one we have proposed for the reduction of $SOCl_2$ by metal phthalocyanines [18]. According to this model, adsorption or chemisorption of the SO_2Cl_2 to the metal catalyst lowers the activation energy for the electron transfer process. On the other hand, it may be argued that the presence of the catalyst merely provides more sites for the adsorption of SO_2Cl_2 onto cathode surface, thereby increasing the concentration of the SO_2Cl_2 being reduced. The net effect of this is a lower effective current density per unit cathode mass and, therefore, lower cathode polarization. Further work is required to distinguish between the two possibilities.

4. Conclusions

The performance of the Li/SO_2Cl_2 cell was evaluated as a function of variables such as the cathode type, electrolyte additives and cathode catalysts. Substitution of the low surface area Chevron carbon by the high surface area Ketjenblack carbon improved both the capacity and load voltage of the Li/SO_2Cl_2 cell. However, this improvement was penalized substantially by the inferior storage properties of Li/SO_2Cl_2 cells containing the high surface area carbon cathode; for example long voltage delay and loss of load voltage and capacity were observed after storage at 70° C for two weeks. The voltage delay improved with the use of carefully purified SO_2Cl_2 and with the addition of Ca^{2+} to the electrolyte. Addition of Ca^{2+} as $Ca(AlCl_4)_2$ especially reduced the voltage delay in cells containing the high surface area carbon cathode. Sulphur dioxide increases the conductivity of $SO_2Cl_2-LiAlCl_4$ electrolyte and it also appears to improve the storability and low temperature discharge performance of Li/SO_2Cl_2 cells. Cathodes doped with a mixture of polyacrylonitrile and Co, Ni or Fe acetate, followed by pyrolysis at 800° C, exhibited about 350–500 mV higher load voltage than uncatalysed cathodes. These new catalysts are effective alternatives to the more expensive catalysts such as platinum and transition metal macrocyclic complexes. Catalysed cells stored at 70° C retained their higher voltage but, like the uncatalysed cells showed a loss in capacity. The cobalt and nickel catalyst, however, did not affect the voltage delay properties of the cell. The Li/SO_2Cl_2 cell appears to be useful for a variety of consumer and military applications.

Acknowledgement

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