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Rechargeable Lithium-Inorganic Electrolyte Cell

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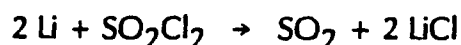
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INTRODUCTION

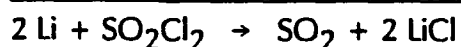
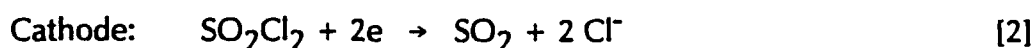
Because of its high energy density (225 Wh/lb), the lithium-sulfuryl chloride system has been studied extensively (1,2) as an alternate of primary lithium-thionyl chloride electrochemical cells. Gilman and Wade (3) examined the discharge characteristics of primary Li/SO₂Cl₂ cells in 1.5M LiAlCl₄ electrolyte using different carbon cathodes and established the following reactions:



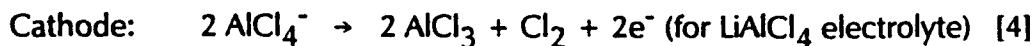
Based on cyclic voltammetry results and the work of Gilman and Wade (3), Behl (4) concluded that the mechanism of cathodic reduction involved first the reduction of free chlorine resulting from the homogeneous and/or heterogeneous dissociation of sulfuryl chloride (5) followed by the reduction of undissociated sulfuryl chloride. Klinedinst and Gary (2) examined primary Li/SO₂Cl₂ system with LiGaCl₄ electrolyte and observed relatively insignificant anode corrosion.

The nature of the discharge reaction and the fact that sulfuryl chloride can be prepared by the reaction of sulfur dioxide and chlorine on carbon have encouraged researchers (6,7) to examine the rechargeability of Li/SO₂Cl₂ systems. Razzini et al (6), while investigating the characteristics of primary Li/SO₂Cl₂ cells, observed some potential rechargeability of the system. Later, Smith and co-workers (7) confirmed the observation and proposed the following discharge-charge reactions:

Discharge Reactions:



Charge Reactions:



Chemical recombination of sulfur dioxide formed on discharge and chlorine formed on charge regenerate the original solvent:



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While AlCl_3 combines with LiCl formed during discharge to regenerate the electrolyte salt:



The sum of the charge and regeneration reactions gives



the reverse of the discharge reaction.

The Li cycling efficiencies in $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$ were examined by Walker and Binder (8) at different rates and observed >80 percent efficiency at current density >5 mA/cm^2 . The authors also examined the effect of the addition of SO_2 and Cl_2 to the electrolyte on Li cycling efficiency.

The overall objective of the present contract research is to develop and improve performance of $\text{Li}/\text{SO}_2\text{Cl}_2$ rechargeable cells with particular emphasis on:

- i) Safety
- ii) discharge capacity, and
- iii) cycle life.

In order to achieve these objectives our approach is to investigate the chemistry of $\text{Li}/\text{SO}_2\text{Cl}_2$ system with different carbon cathode materials, to optimize the cathode structure, to minimize the anode corrosion problem and to examine the effects of electrochemical parameters on cycle performance.

EXPERIMENTAL

Experimental cells with a flat electrode design were used to study the cell chemistry and cycling performance of the $\text{Li}/\text{SO}_2\text{Cl}_2$ system in 1.5M LiGaCl_4 and 1.5M LiAlCl_4 electrolytes. The positive carbon electrodes were made by mixing proper amounts of carbon, Teflon, alcohol and water to form a dough. The dough was then rolled to a thickness of about .020-.030 inch and air-dried in a dry room. The rolled carbon sheet was then cut to a proper dimension of the cathode and pressed on both sides of a Teflon-rich carbon coated perforated Ni-foil (.005 inch thick). The resulting cathode was then dried and cured at 150°C under vacuum for 30 minutes.

The lithium anodes were made by pressing two layers of lithium foil (.010 inch) on each side of a .005 inch perforated Ni-foil. The cell configuration was as follows:

Anode/Separators/Cathode/Separators/Anode

The positive carbon electrode was positioned in the center and sandwiched between two negative lithium electrodes and separated by non-woven glass paper and microporous Tefzel. The cell system was packed in a Tefzel (.002 inch thick, 60% porous) bag to prevent shorting to the can while permitting electrolyte diffusion.

The design specifications of hermetically sealed experimental Li/SO₂Cl₂ cells are summarized in Table 1. The exploded view of cell components and stack assembly are shown in Figure 1. The cell stack was placed between two half cylindrical Teflon shims and inserted in "D" size stainless steel cans. Several cells were built with a Li reference electrode. In this case, a 5/4-D can with both ends opened was used. The positive electrode was connected to the can and the negative and reference electrodes to the top and bottom center posts of the glass-metal seal by welded nickel tabs. The cell was sealed by welding the top and bottom to the can using a LASER welder. The cell was then vacuum-filled with the electrolytes.

Both 1.5M LiAlCl₄/SO₂Cl₂ and 1.5M LiGaCl₄/SO₂Cl₂ electrolytes were used to evaluate the Li/SO₂Cl₂ cell performance. The electrolytes were prepared from their individual salts, LiCl (Baker Analytical Reagent, 99.3%), AlCl₃ (King's Mountain, >99.9% pure from our analysis) and GaCl₃ (Eagle Pitcher, 99.999%). LiCl was dried at 120°C under vacuum for at least 24 hours. AlCl₃ and GaCl₃ were used as received. The solvent SO₂Cl₂ was obtained from Alfa Products with claimed purity of 99%. The electrolytes were stored under Li-chips for at least 24 hours prior to activation of the test cells. The concentrations of the electrolyte solutions were checked by Direct Current Plasma (DCP) Spectroscopy.

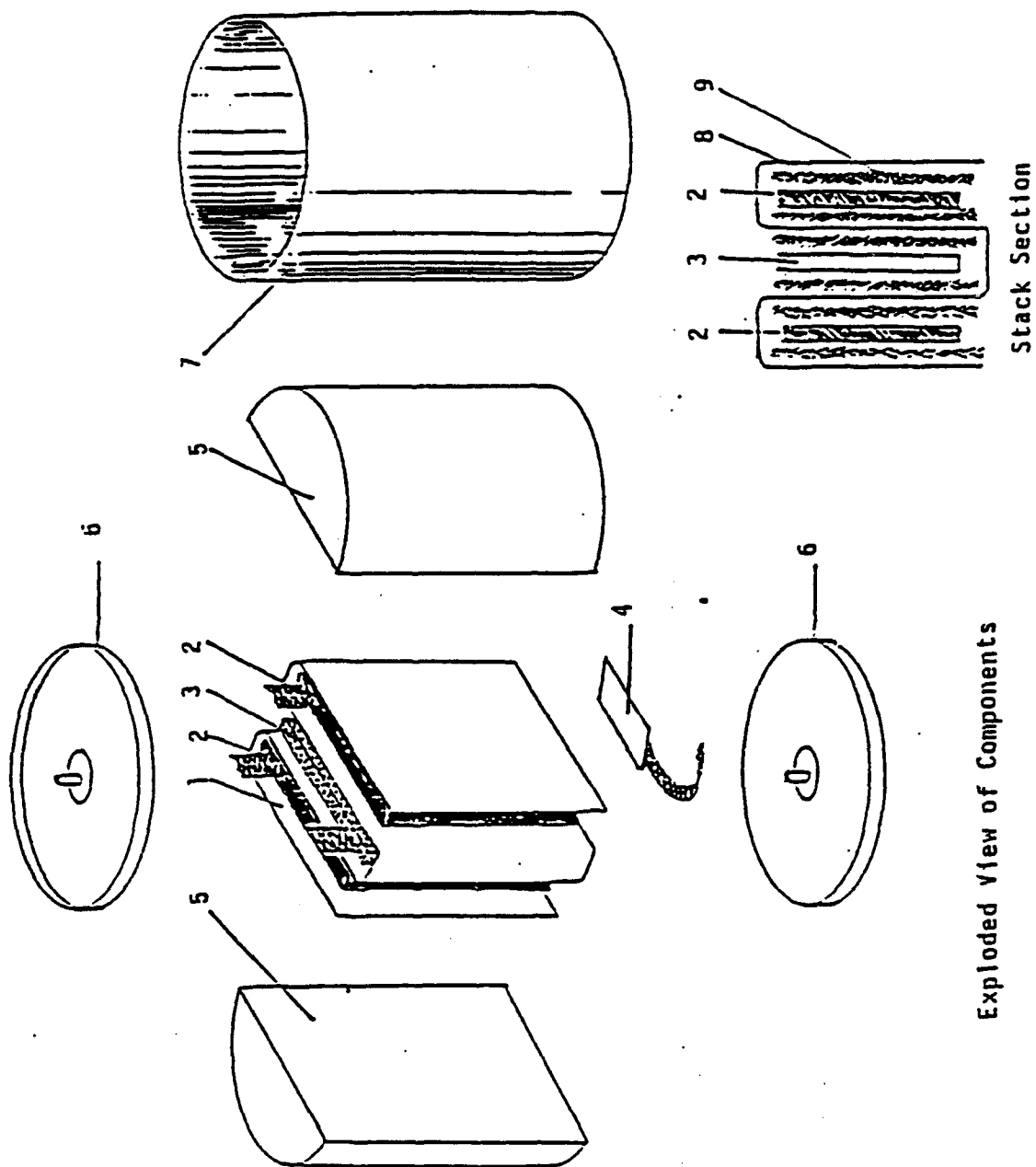
RESULTS AND DISCUSSION

The performance of twelve hermetically sealed experimental Li/SO₂Cl₂ cells containing Ketjen Black (L001-L003) and mixed carbon cathodes in 1.5M LiAlCl₄ (L001-L005 and L012) and 1.5M LiGaCl₄ (L006-L011) electrolytes are summarized

Table 1

Design Specifications of Experimental Li/SO₂Cl₂ Cells

Cathode:	Carbon and PTFE rolled, dried and then pressed on Teflon-rich carbon coated perforated Ni foil (.006")		
Anode:	.010" Li foil roll-pressed on each side of .006" perforated Ni foil		
Reference:	Same as anode		
Electrolyte:	1.5M LiAlCl ₄ /SO ₂ Cl ₂ and 1.5M LiGaCl ₄ /SO ₂ Cl ₂		
Separator:	Porous glass fiber (Lectromat); Tefzel (Scimat)		
Cathode:	Area	25 cm ²	
	Thickness	0.04-0.07 cm	
	Weight	0.13-0.35 g	
Anode:	Area	25 cm ²	
	Thickness	0.05 cm	
	Weight	0.70 g	
	Capacity	2.7 Ah (Theoretical)	



Exploded View of Components

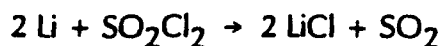
Stack Section

Hermetically Sealed Rechargeable Stack Assembly

- | | |
|------------------|---------------------|
| 1. Separator | 6. Case Cover |
| 2. Anode | 7. Case |
| 3. Cathode | 8. Tefzel Separator |
| 4. Li Reference | 9. Glass Separator |
| 5. Teflon Spacer | |

in Table 2. All twelve cells show an open circuit potential of about 3.9 V. The cells were examined at 1-5 mA/cm² discharge and 1-2 mA/cm² charge rates within the voltage limits of 2.5-4.2 V and the time limits of 4 to 50 hours.

The discharge-charge characteristic of a Li/SO₂Cl₂ cell (L003) containing Ketjen Black cathode and 1.5M LiAlCl₄ electrolyte is shown in Figure 2. The cell suffered from a significant voltage delay due to anode passivation. Similar voltage delay behavior of Li/SO₂Cl₂ primary cells was observed by others (2) and was interpreted as due to the formation of a relatively thick layer of LiCl on the anode surface.



Anode polarization is measured by subtracting the potential difference between the cathode and reference ($E_c - E_R$) from the cell voltage ($E_c - E_L$). The anode polarization is significant at the beginning of the discharge due to anode passivation and then gradually decreases as the passive layer breaks down until the cell attains a flat discharge behavior. During charge, the cell shows no increase in voltage but capacity gradually decreases with time, indicating inefficient charge. The probable reason for this is discussed below. The cell was discharged within the time limit of 6 hours and delivered a capacity of 3.31 Ah/g of carbon.

At the beginning of the second discharge cycle, the cell reaches the lower voltage limit immediately because of inefficient charge and severe anode passivation.

Two other cells (L001-L002) with Ketjen Black carbon and LiAlCl₄ electrolyte show similar voltage delay an discharge-charge behavior even at low discharge (1 mA/cm²) rate (L001).

Two cells were made with blended carbon (80% low surface area Shawinigan Acetylene Black + 20% high surface area Cabot Black Pearls 2000) and activated with LiAlCl₄ electrolyte (L004 and L005). Both of these cells showed much less voltage delay but were unable to cycle.

A typical discharge-charge behavior of cell L004 is shown in Figure 3. The cell was discharged at 1 mA/cm² by the time limit of 30 hours and delivered a capacity of 2.16 Ah/g of carbon.

Table 2
Li/SO₂Cl₂ Cell Performance

Cell No.	Cathodes	Electrolytes	Cycling Conditions		Discharge/ Charge Time Limit (Hours)	Discharge Capacity (Ah/g Carbon)	
			Voltage Limits (V)	Discharge/ Charge Rate (mA/cm ²)		1st	2nd
L001	92% a + 8% TFE	1.5M LiAlCl ₄	2.5-4.2	1.0/1.0	30/30	3.06	-
L002	"	"	3.0-4.2	5.0/1.0	6/30	3.20	1.71
L003	"	"	2.5-4.2	5.0/1.0	6/30	3.31	-
L004	80% b + 20% c + 4% TFE	"	2.5-4.2	1.0/1.0	30/30	2.16	-
L005	"	"	3.0-4.2	5.0/1.0	6/30	2.01	-
L006	"	1.5M LiGaCl ₄	3.0-4.2	1.0/1.0	50/50	2.49	-
L007	"	"	3.0-4.2	5.0/1.0	4/20	1.44	-
L008	"	"	2.5-4.2	5.0/2.0	4/10	1.46	-
L009	"	"	2.0-4.2	Cell failed to discharge	Failed to Cycle	Failed to Cycle	-
L010	"	"	3.0-4.2	1.0/1.0	50/50	2.52	-
L011	"	"	3.0-4.2	2.0/1.0	16/30	2.49	-
L012	"	1.5M LiAlCl ₄	3.0-4.2	5.0/1.0	6/30	1.91	-

a-Ketjen Black

b-Shawinigan Acetylene Black

c-Black Pearl

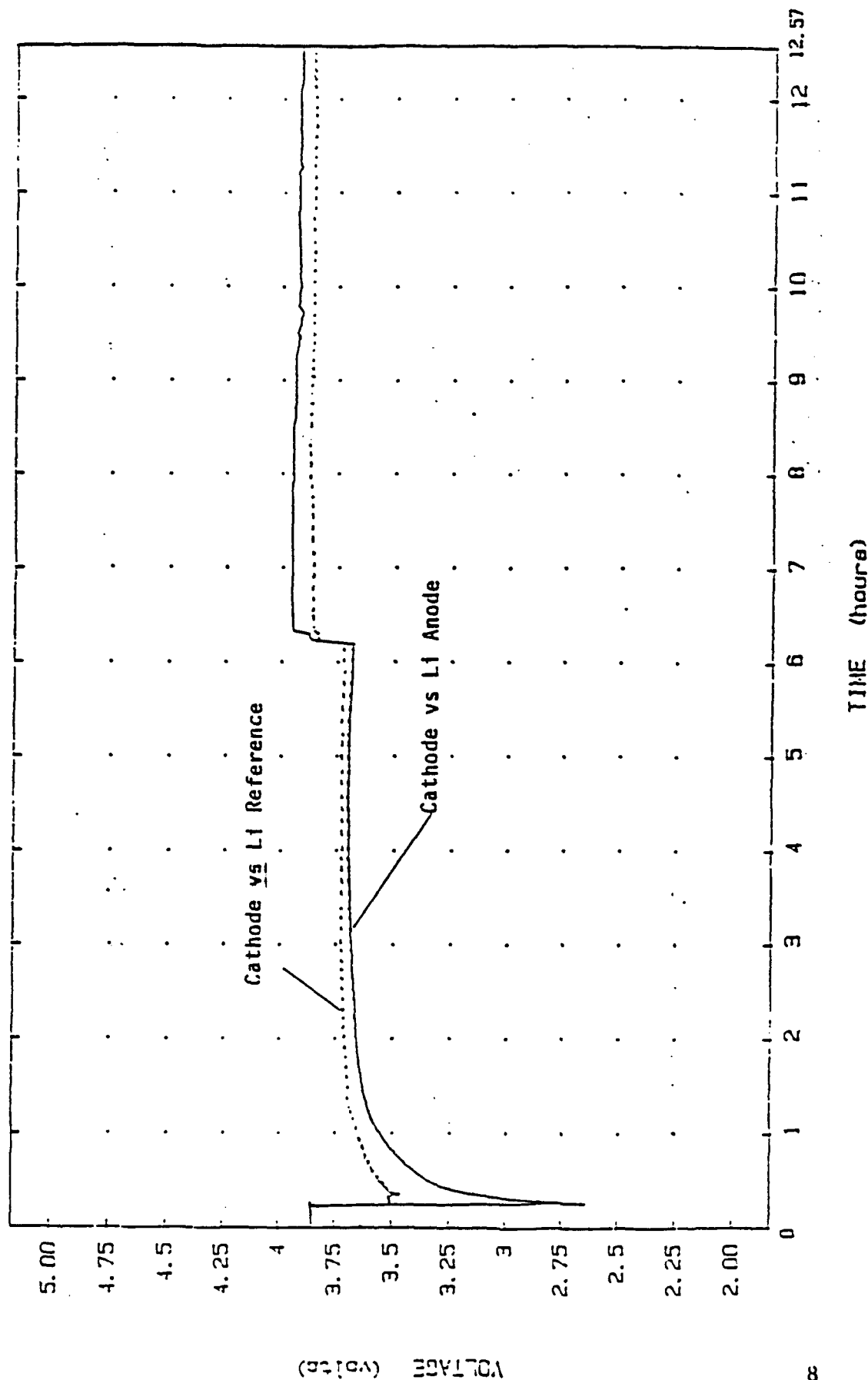


Figure 2. Polarization Behavior of Li/SO₂Cl₂ Cell (#L003) in 1.5M LiAlCl₄/SO₂Cl₂ Electrolyte at 5 mA/cm² Discharge and 1 mA/cm² Charge Rates. Voltage Limits: 2.5-4.2V. Cathode Area: 25 cm².

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CELL NO. L004

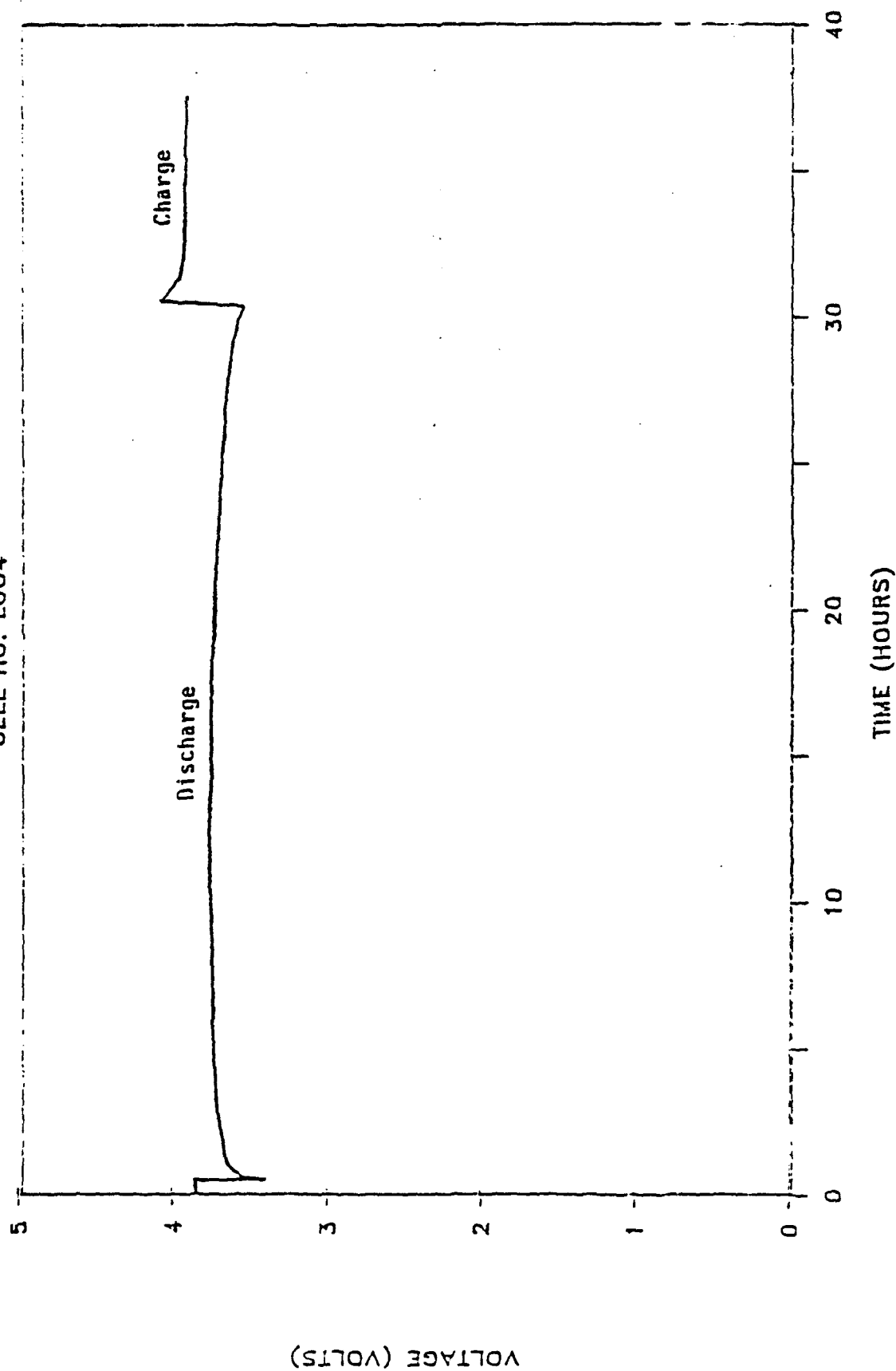


Figure 3. Discharge-Charge Behavior of a Li/SO₂Cl₂ Experimental Cell (#L004) in 1.5M LiAlCl₄/SO₂Cl₂ Electrolyte at 1.0 mA/cm² Discharge and Charge Rates. Voltage Limits: 3.0-4.0V. Time Limit: 30 hours. Cathode and Anode Area: 25 cm².

Cells made with blended carbon cathode and LiGaCl_4 electrolyte show significantly lower voltage delay (Figure 4) at 1 mA/cm^2 discharge and charge rate. Even at a higher discharge rate (5 mA/cm^2) the system shows insignificant voltage delay.

All twelve cells experienced inefficient charging and hence were unable to cycle. Charging will be inefficient if the Cl_2 and AlCl_3 generated in reaction [4] fail to undergo reactions [5] and [6] but instead, diffuse to and attack the Li electrode as in [8].



which will also cause anode passivation. In our system, inefficient charging might have occurred due to the use of microporous Tefzel separator. Similar inefficient cycling was observed by Smith and James (9) when they used Tefzel separator in their $\text{Li/SO}_2\text{Cl}_2$ system. From our study we may conclude that:

- (i) High surface area carbon has significant influence on anode passivation in $\text{Li/SO}_2\text{Cl}_2$ system;
- (ii) anode passivation is more significant with LiAlCl_4 than LiGaCl_4 electrolyte;
- (iii) Tefzel separator may cause inefficient charging.

FUTURE WORK

The following work is planned to do in the next quarter:

- (i) The effect of different carbons on $1.5\text{M LiAlCl}_4/\text{SO}_2\text{Cl}_2$ using electrolyte by IR Spectroscopy;
- (ii) Evaluation of cycling performance of different $\text{Li/SO}_2\text{Cl}_2$ cells with glass rather than Tefzel separator.
- (iii) Allow cells to drop below cutoff voltage to accommodate the voltage delay.

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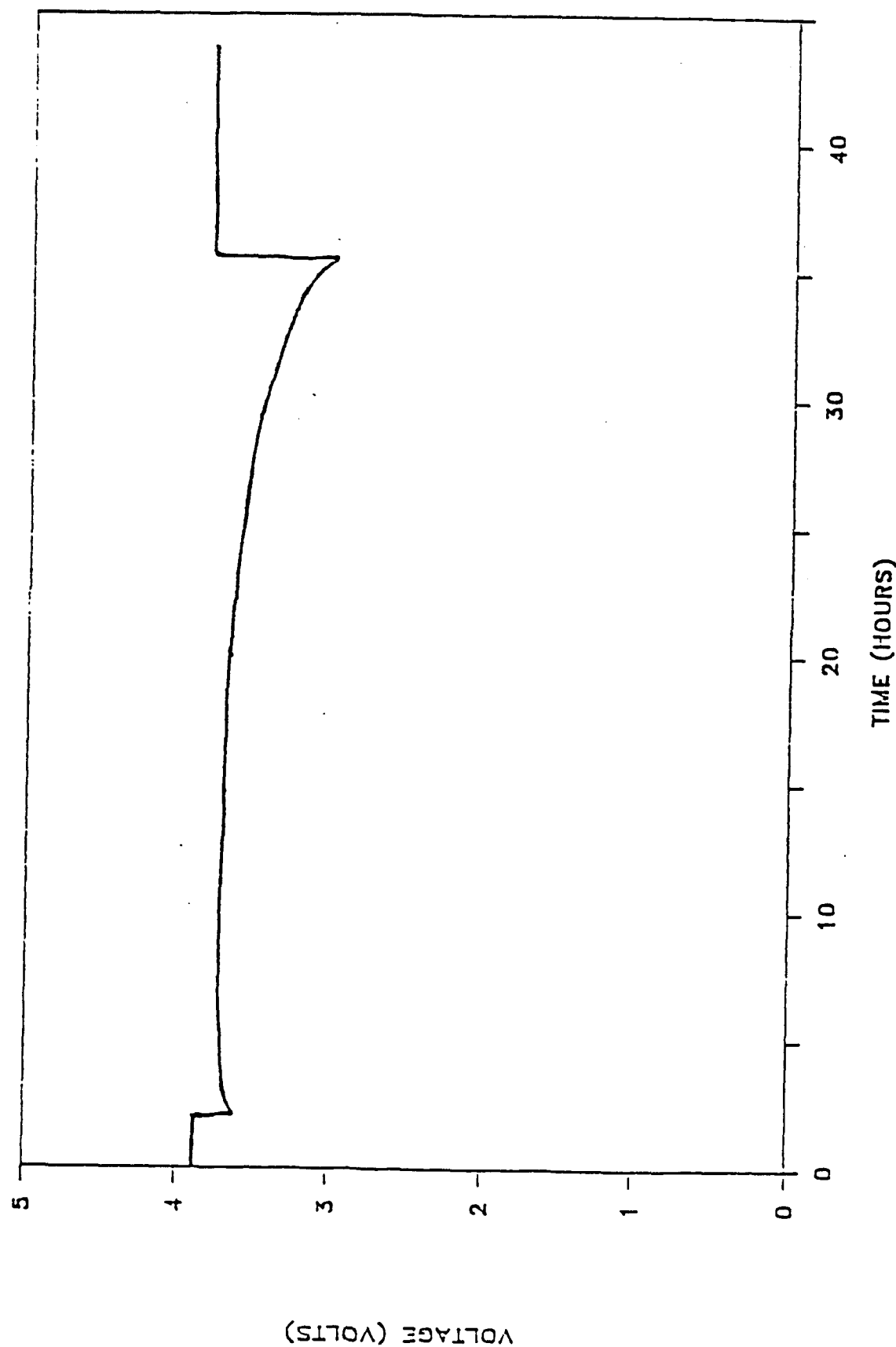


Figure 4. Discharge-Charge Behavior of a Li/SO₂Cl₂ Experimental Cell (#L010) in 1.5M LiGaCl₄/SO₂Cl₂ Electrolyte at 1.0 mA/cm² Discharge and Charge Rates. Voltage Limits: 3.0-4.2V. Cathode Area: 25 cm².

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