

REDUCTION OF VOLTAGE DELAY IN THE Li/SOCl₂ SYSTEM — A STUDY OF POLYMERS WITH CHLORINE SUBSTITUENT GROUPS AS DELAY REDUCING ADDITIVES

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Summary

Several kinds of vinyl polymers with chlorine substituent groups have been evaluated as voltage-delay reducing additives. The reduction of the voltage delay was affected by the properties of substituent groups, and polyvinyl chloride (PVC) and vinyl chloride-vinylidene chloride copolymer exhibited excellent performance. Observations using energy dispersive X-ray analysis, scanning electron microscopy, and impedance analysis indicate that the growth of the LiCl passivating film is slowed by the polymer film formed on the lithium anode in the PVC-added electrolyte.

Introduction

The Li/SOCl₂ cell system, by virtue of its high voltage and high energy density, has attracted considerable interest in many applications. However, a major problem in high-rate applications is the voltage delay phenomenon. It is well known that an LiCl passivating film is formed on the lithium surface when it comes into contact with the SOCl₂ electrolytic solution. This film reduces any chemical interaction between the lithium and the SOCl₂, but causes a temporary voltage depression under a heavy load, especially when cells are discharged after extended storage periods.

Various kinds of new electrolyte salts (*e.g.*, Li₂B₁₀Cl₁₀ [1], Li₂O-AlCl₃ [2] and Li₂S-NbCl₅ [3]) and additives (*e.g.*, vinyl polymer [4, 5] and cyanoacrylate [6]) have been suggested for reducing the voltage delay. The LiCl film morphology and the mechanism of the reduction in the voltage delay have both been investigated [5 - 7].

When a polymer is used as a voltage-delay reducing additive, it is considered that the extent of reduction depends on the features of the polymer, *e.g.*, substituent groups, polymer structure and/or the degree of polymerization. This paper reports the effect of various vinyl polymers with chlorine substituent groups. The mechanism for the reduction of voltage delay has been studied.

Experimental

Eight polymers were investigated; these are listed in Table 1. Six polymers have different chlorine contents, ranging from 0% (polyethylene) to 73.1% (polyvinylidene chloride), and have different molecular weights and structures. The remaining two polymers (chlorinated polypropylene and rubber chloride) have electron-donating methyl groups ($-\text{CH}_3$) on the opposite sides of the chlorine groups.

TABLE 1
Evaluation of polymers as delay reducing additives

Polymer	Structural formula	Chlorine content	Molecular weight
Polyethylene (PE)	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$	0%	24000
Chlorinated polyethylene (CPE)	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_l \left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_m \left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right)_n$	40%	>100000
Polyvinyl chloride (PVC)	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_n$	56.7%	65000
Vinyl chloride-vinylidene chloride copolymer (VC-VDC)	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_m \left(\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_n$	58.6%	28000
Chlorinated polyvinyl chloride (CPVC)	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_l \left(\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_m \left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right)_n$	69.5%	120000
Polyvinylidene chloride (PVDC)	$\left(\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_n$	73.1%	100000
Chlorinated polypropylene (CPP)	$\left(\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right)_n$	66.2%	43000
Rubber chloride (RC)	$\left(\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \quad \quad \quad \\ (\text{Cl}) \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array} \right)_n$	> 65%	10000

Of the eight polymers selected, polyethylene was obtained from Seitetsu Kagaku Co., Ltd.; chlorinated polyethylene from Showa Denko Co., Ltd.; polyvinyl chloride and vinyl chloride-vinylidene chloride copolymer from Denki Kagaku Kogyo Co., Ltd.; chlorinated polyvinyl chloride from Nippon Carbide Industries Co., Inc.; polyvinylidene chloride from Asahi Kasei Kogyo Co., Ltd.; chlorinated polypropylene from Sanyo Kokusaku Pulp Co., Ltd.; and rubber chloride from Asahi Denka Co., Ltd..

Polymers were used as received. Each polymer powder was added to a 1.2 M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte at a concentration of 2.5 g l^{-1} and was stirred. All of them, except polyethylene and chlorinated polyethylene, dissolved completely. Polyethylene powder was finely dispersed in the electrolyte and a small amount of chlorinated polyethylene remained undissolved.

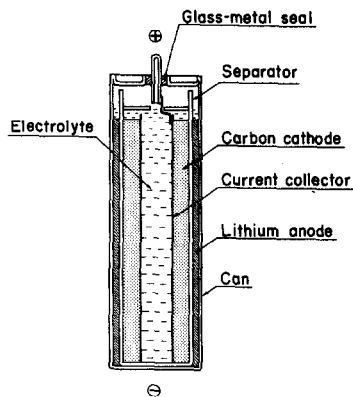


Fig. 1. Cross sectional view of a bobbin type AA-size cell.

The voltage delay and other discharge characteristics were evaluated in AA-size cells with hermetic glass-to-metal seals, as shown in Fig. 1. The cathode was a highly porous bobbin cathode, using acetylene black and a PTFE binder. The outer diameter of the cathode was 10 mm and the height was 40 mm. The anode was made by pressing a lithium foil onto a stainless steel can and the surface area was 14.8 cm^2 .

The voltage delay and other discharge characteristics were evaluated measured using a Solartron 1250 Frequency Response Analyzer. After being stored for 20 or 40 days (60°C), or for 6 months (20°C), voltage delay tests were performed using 30Ω resistive loads, followed by discharge under the same loads to evaluate the discharge capacities.

A lithium strip was immersed for 5 h in an SOCl_2 electrolyte containing an additive. It was then removed and rinsed with clear thionyl chloride. The sample was allowed to dry and was examined with a JEOL JSM-T200/SEIKO DENSHI SED/880 EDX (energy dispersive X-ray) analyzer.

Results and discussion

Voltage delay has two components: (i) an initial voltage depression when a cell is placed on load; (ii) the time required for the voltage to recover to its operating level [6]. Figure 2 shows the voltage-delay characteristics — initial minimum voltage and recovery time for the voltage to 2.5 V — for various cells with different additives.

Among the eight polymers evaluated, polyvinyl chloride (PVC) and vinyl chloride-vinylidene chloride copolymer (VC-VDC) exhibited excellent reducing effects, *i.e.*, high initial voltage and fast voltage recovery time. A cell with chlorinated polyvinyl chloride (CPVC) also exhibited a marked reduction in the voltage delay after storage at 60 °C for 20 days and 6 months at 20 °C, but, after 40 days storage at 60 °C, the voltage recovery time was slightly longer than that for PVC and for VC-VDC. On the other hand, no improvement was observed with cells containing either polyethylene (PE) or chlorinated polyethylene (CPE), which had smaller chlorine contents than PVC. In the case of polyvinylidene chloride (PVDC), where chlorine groups are on both sides of a carbon atom, the voltage delay was slightly reduced. Chlorinated polypropylene (CPP) and rubber chloride (RC) also showed no delay-reducing effects, while the initial voltage depression for a cell with RC was not significant. Hence, the reduction of the voltage delay was shown to be influenced by the properties of the substituent groups.

Results of a.c. impedance measurements are presented in Fig. 3. The Cole-Cole plot of the cell impedance exhibited a semi-circle in the 0.1 - 65 000 Hz frequency region (curve (a)). The value of parameter θ , which is considered to represent the anode characteristics, increased with storage time, as shown in curve (b). The impedance behaviour of the cell with CPE, which showed no improvement in the reduction of the voltage delay, was almost the same as that for a cell with no additive, and the value of θ was 795 Ω after 20 days storage at 60 °C. By contrast, the increase in the im-

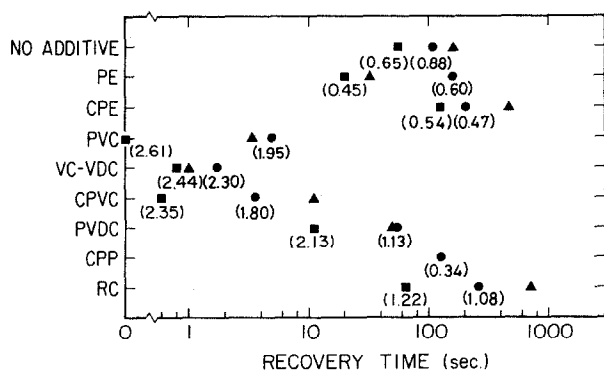


Fig. 2. Voltage-delay characteristics for various cells with different additives (average of 3 - 6 measurements, 30 Ω): ●, 20 days storage at 60 °C; ▲, 40 days storage at 60 °C; ■, 6 months storage at 20 °C. Values in parentheses indicate initial minimum voltages.

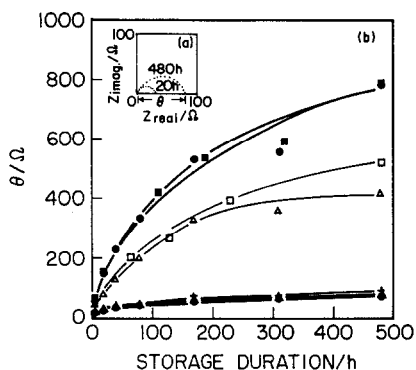


Fig. 3. Impedance increase for cells with different electrolytes: (a) impedance diagram for PVC added cell, 60 °C storage; (b) increase in θ as a function of storage time: ●, no additive; ■, CPE; ▲, PVC; ○, VC-VDC; +, CPVC; △, PVDC; □, RC.

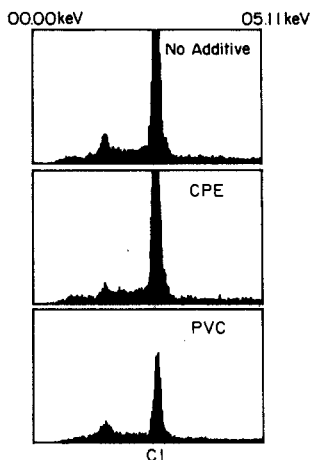


Fig. 4. EDX spectra for lithium surface; 5 h storage at room temperature.

pedance of the cell with reduced voltage delay was very small. The value of θ was only 80 Ω in the case of the dissolved PVC cell after being stored at 60 °C for 20 days. This result suggests that the growth of the LiCl passivating film was retarded in the dissolved PVC (and/or VC-VDC, CPVC) electrolyte, compared with those in the other solutions.

Figure 4 shows EDX spectra for lithium samples stored for 5 h at room temperature in different electrolytes. The observed Cl peaks are considered to be attributable to the LiCl passivating film formed on the lithium surface, because the Al and S peaks ascribed to LiAlCl_4 and SOCl_2 were not detected. The Cl peak for the sample immersed in the dissolved PVC electrolyte is smaller than those for the other two samples. In the case of CPE added electrolyte, the Cl peak is almost as great as that observed in the absence of an additive. The LiCl film growth rate on the anode was found to be reduced in the dissolved polyvinyl chloride electrolyte, but not in the chlorinated polyethylene-containing electrolyte.

A lithium strip was stored in the dissolved PVC electrolyte for 5 h. It was then removed, rinsed carefully with SOCl_2 and dried. The sample was then immersed in ethanol. A very thin polymer film was obtained after the lithium had dissolved completely. This film had a rugged surface with many small holes of different sizes, as shown in Fig. 5. The thickness of the film, measured from the depth of a hole in the micrograph, was about 1.5 μm . In the case of VC-VDC or CPVC dissolved electrolyte, a thin polymer film was also obtained. By contrast, no polymer film was produced on the lithium strips stored in the dissolved PE, CPE or CPP electrolytes.

It appears that polyvinyl chloride, dissolved in the electrolyte, sticks to the lithium anode in the form of a film due to an affinity between the

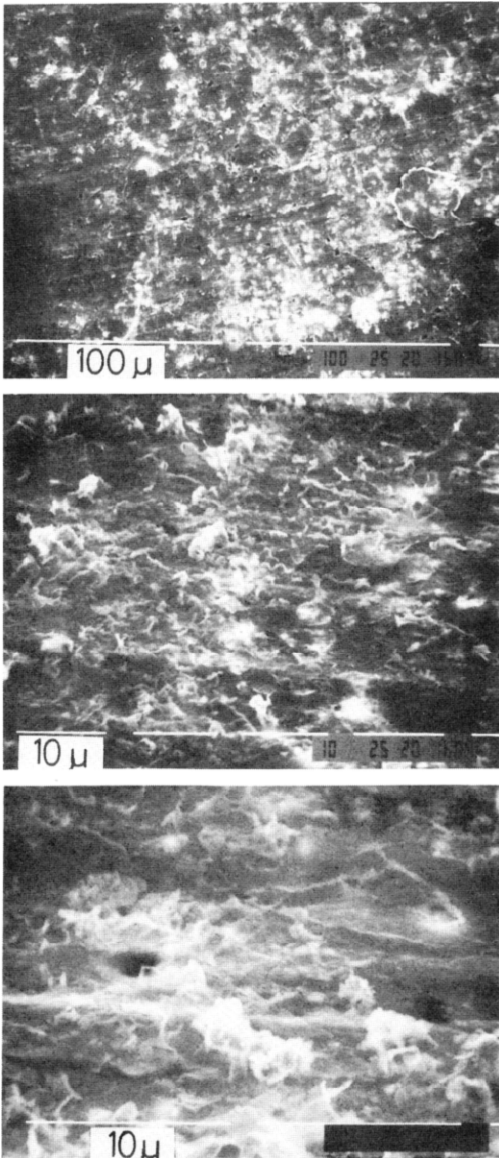


Fig. 5. Polymer film obtained after lithium has been dissolved in ethanol.

chlorine group and lithium and, consequently, it slows the growth of an LiCl film and changes the film morphology. The chlorine content of chlorinated polyethylene is less than that of PVC. In the case of chlorinated polypropylene, the extent of electron withdrawal for the chlorine group is reduced by the electron transfer from CH_3 to Cl. Therefore, the affinity between the polymer and lithium is thought to weaken, and thereby to yield no improvement in the voltage delay.

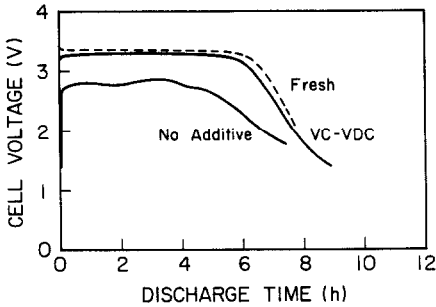


Fig. 6. Discharge characteristics for AA-size batteries; fresh (dotted line) and 40 days storage at 60 °C, 30 Ω .

The degree of polymerization of a polymer is considered to be another important factor in determining the voltage delay reduction. Further studies are needed in this area.

Figure 6 shows discharge characteristics for fresh and stored cells. After 40 days storage at 60 °C, the cell with VC-VDC in solution showed more promising characteristics (*i.e.*, a longer discharge duration and a higher discharge voltage) than a cell using no additive. In the case of the cell without additives, the capacity at high-rate discharge was small due to the anode passivation. Moreover, the cell with reduced voltage delay exhibited little capacity loss after storage. It is reasonable to speculate that the addition of a polymer to reduce voltage delay does not result in accelerated corrosion of the lithium anode.

Conclusions

- (i) Eight polymers with chlorine substituent groups have been evaluated as voltage-delay reducing additives, and polyvinyl chloride and vinyl chloride-vinylidene chloride copolymer have exhibited excellent reducing effects.
- (ii) Voltage delay reduction is affected by the properties of substituent groups.
- (iii) Polyvinyl chloride, which is dissolved in the electrolyte, is considered to stick to the lithium anode in the form of a film, due to an affinity between the lithium and the electron-withdrawing chlorine group. This polymer film slows the growth of the LiCl-passivating film and changes the film morphology.
- (iv) A cell with reduced voltage delay shows more promising discharge characteristics than a cell without additives.

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