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## An Aluminum/Chlorine Rechargeable Cell Employing a Room Temperature Molten Salt Electrolyte

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### ABSTRACT

A novel Al/Cl<sub>2</sub> rechargeable electrochemical cell is described which employs an Al negative and graphite positive electrode in a room temperature molten salt electrolyte of 1.5:1 AlCl<sub>3</sub>:1,2-dimethyl-3-propylimidazolium chloride. The graphite positive electrode functions as a reversible intercalation electrode for chlorine, eliminating the need for separate anolyte and catholyte compartments. The cell possesses an average discharge voltage of 1.7V for currents of 1-10 mA/g graphite and over 150 cycles at 100% depth-of-discharge for positive electrode limited cells have been demonstrated. Improvements in the chlorine storage capacity of the positive electrode are needed to obtain satisfactory energy densities.

The development of new high energy density secondary batteries continues to be an active research area. Problems with lithium-based systems due to the highly reactive nature of freshly deposited Li have prompted research on alternative electrode systems. Aluminum is an attractive electrode material because of its high electrochemical equivalent weight (2.98 Ah/g), leading to high theoretical gravimetric and volumetric energy densities. Chloroaluminate molten salts which remain liquid at ambient temperatures can be obtained from mixtures of aluminum chloride and organic quaternary salts, particularly 1-methyl-3-ethylimidazolium chloride (MEIC) (1). High cycling efficiencies for Al have been demonstrated in acidic AlCl<sub>3</sub>:MEIC melts (2), suggesting that these electrolytes may be useful for secondary batteries employing a reversible Al electrode.

The feasibility of employing room temperature chloroaluminates as battery electrolytes has been demonstrated for several primary cells and, more recently, secondary cells. The application of AlCl<sub>3</sub>:MEIC molten salts for battery electrolytes was first illustrated with a primary cell based on an Al anode coupled with an FeCl<sub>3</sub> cathode (3). A concentration cell employing Al electrodes in separate basic anolyte and acidic catholyte melts was demonstrated, giving discharge voltages of 1.0-1.3V at currents up to 0.5 mA/cm<sup>2</sup> (4). Piersma and Wilkes (5) studied a number of electrode materials and cations for possible use in secondary cells employing room temperature molten salts. Several primary and secondary cells were recently employing AlCl<sub>3</sub>:MEIC electrolytes (6), particularly a Cd/Br<sub>2</sub> reversible cell (7, 8).

However, the secondary cells reported to date require anolyte and catholyte solutions of different compositions separated by an ion-exchange membrane. Such a system requires relatively large volumes of melt, resulting in a lower energy density (2). The need for leak-free seals and the cost of ion-exchange membranes would pose technical problems in the construction of practical low cost batteries.

We recently reported the development of a room temperature molten salt based on 1,2-dimethyl-3-propylimidazolium chloride (DMPriCl) and AlCl<sub>3</sub> that possesses favorable properties for a battery electrolyte (9). This report describes a new secondary electrochemical cell employing a 1.5:1 AlCl<sub>3</sub>:DMPriCl melt electrolyte with an Al

negative electrode and graphite positive electrode, where the graphite serves as a reversible chlorine intercalation electrode. Since the chlorine reaction product is stored by intercalation, the need for separate anolyte and catholyte compartments is eliminated. Over 150 cycles at 100% depth-of-discharge (DOD) of the positive electrode have been obtained for this cell with an average discharge voltage of ca. 1.7V under various discharge conditions.

### Experimental

The DMPriCl salt was prepared as previously described (9). The 1.5:1 AlCl<sub>3</sub>:DMPriCl electrolyte was prepared by slow addition of a weighed amount of sublimed AlCl<sub>3</sub> (Fluka Chemical Company, puriss. grade) to DMPriCl using an airless addition funnel (SGA Scientific) while cooling in liquid N<sub>2</sub>. The mixture was then allowed to warm slowly to room temperature while stirring. All subsequent handling of the melt was carried out in an Ar-filled glove box (Vacuum Atmospheres Corporation). Melts were purified by electrolyzing between two Al rods (Alfa, Puratronic grade) at a current of 100 μA for several days or until the electrodes remained shiny for a day during electrolysis.

Aluminum electrodes were cut from high purity 0.13 mm Al foil (Alfa) into approximately 1 × 4 cm rectangles and an Al wire contact attached by spot welding. Prior to use, the electrodes were cleaned in H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub>, rinsed with water and alcohol, and vacuum dried.

Graphite electrodes were prepared from -100 mesh graphite powder (Ultra Carbon Corporation) with 10 weight percent polysulfone as binder. Polysulfone was dissolved in methylene chloride and the graphite dispersed by rapid stirring. Rapid addition of acetone results in the precipitation of a graphite + binder "putty." This putty was spread onto a Mo screen (Rembar Company) of ca. 1 × 4 cm and vacuum dried to remove the solvent, forming a bonded electrode. A Pt wire was fed through the screen to provide contact. After drying, the electrode was weighed to determine the weight of active material. Electrodes typically contained 150-250 mg graphite. Charge and discharge currents are reported in current per gram graphite since it was found that cell performance was dependent on the weight of graphite present in the electrode rather than area, for heavily loaded *vs.* thin graphite electrodes.

Cells were constructed from 6 × 10 mm id borosilicate glass rectangular tubing (Vitro Dynamics Incorporated)

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cut to approximately 5 cm length and joined to a glass o-ring connector (Kontes). The cell top consisted of a similar o-ring connector with two Pt wires sealed in glass as contacts and fitted with a vacuum valve. The cell was sealed with a Viton o-ring and pinch clamp (Fig. 1). This design provides a convenient cell which is airtight, allows visual inspection, and can readily be dismantled for post-cycling studies.

The electrochemical cell was constructed by positioning the two electrodes opposite one another separated by a glass fiber separator (Gelman Sciences Incorporated) "Z-folded" to prevent edge shorting. The cell and glass separator were initially dried at 140°C. The assembled cell was evacuated, transferred to the glove box, and filled with approximately 1.5 ml of molten salt electrolyte.

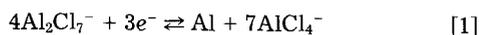
Cells were cycled using either a Model 545 battery tester equipped with a Model 545T timer (Eco Instruments) or by computer control using an HP 1000 computer (Hewlett-Packard) interfaced to a constant current module constructed in-house. The software was a modified version of a battery "soft cycler" previously described (10). Either cycling method allowed independent control of charge and discharge current, time, and voltage limit. Computer cycling further allowed introduction of open-circuit time periods. Cells were typically charged for a predetermined time period followed by full discharge to a cutoff voltage of 0.8-1.0V at equal charge and discharge currents. An open-circuit period of 1h was introduced following charge during computer controlled cycling. Cells were cycled at room temperature unless stated otherwise.

Samples for NMR spectra were prepared by placing the 1.5:1 melt mixed with approximately 20 v/v C<sub>6</sub>D<sub>6</sub> and TMS as internal standard into a 5 mm od NMR tube which was then sealed off with a torch. Proton and <sup>13</sup>C spectra were obtained on a Varian Model XL-400 spectrometer.

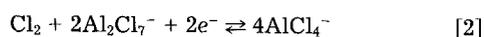
## Results and Discussion

**Cell reactions.**—It was desired to construct an electrochemical cell based on the electrode reactions of Al deposition at the negative electrode (anode) coupled with oxidation of AlCl<sub>4</sub><sup>-</sup> to chlorine at the positive electrode (cathode) during charge, with the reverse reactions occurring during discharge. Such a cell would yield the highest possible cell voltage for an acidic melt since these reactions represent the cathodic and anodic decomposition reactions for this electrolyte (9, 11).

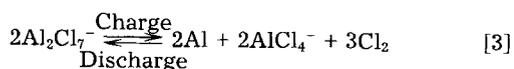
The electrodeposition of Al has been studied in acidic AlCl<sub>3</sub>:alkali chloride molten salts (12) and occurs via the reaction



The chlorine reaction was studied by potentiometry in room temperature molten salts and the electrode reaction determined to be (13)



Combining Eq. [1] and [2] gives for the overall cell reaction



Unless the anolyte and catholyte are separated (a requirement we wished to avoid), a means of storing the chlorine generated on charge is required so that it is available for discharge and to prevent self-discharge due to reaction at the Al electrode. Intercalation electrodes have found wide application in battery systems, and the use of graphite intercalation compounds as electrode materials has been studied (14, 15). Graphite is known to form an intercalation compound with chlorine (16) and hence was investigated for use as a reversible chlorine electrode.

The use of graphite intercalation compounds for chlorine electrodes in molten salt cells was previously studied in NaCl:AlCl<sub>3</sub> (17). The authors propose the electrode reaction to occur as

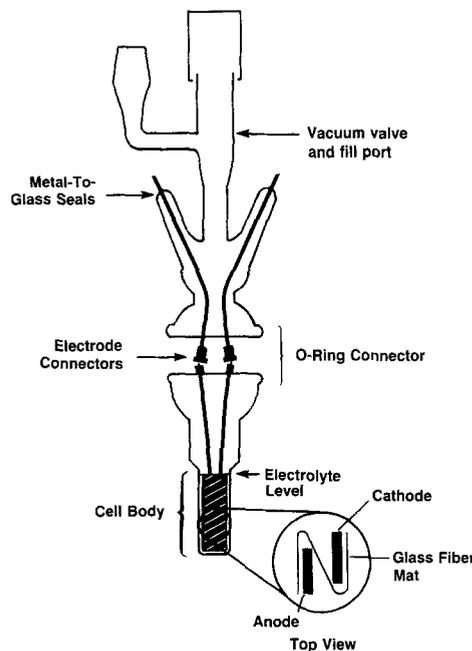
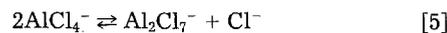
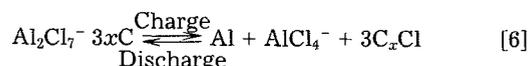


Fig. 1. Schematic of laboratory Al/Cl<sub>2</sub> electrochemical cell

In an acidic melt the Cl<sup>-</sup> product would undergo further chemical reaction due to the equilibrium



Therefore, the cell reactions for an Al/Cl<sub>2</sub> cell can be summarized as electrodeposition of Al and oxidation of AlCl<sub>4</sub><sup>-</sup> to a graphite-chlorine intercalate on charge with the reverse reactions occurring on discharge



As shown by Eq. [3] and [6], the melt composition varies during battery cycling as a result of the electrode reactions. Since Al cannot be electrodeposited from a basic or neutral melt (9), the cell can operate only in the acidic range, imposing an electrolyte limitation on the cell energy density. The cells described here are assembled in a discharged state with a 1.5:1 AlCl<sub>3</sub>:DMPPrCl electrolyte. If we assume that the cell can operate between 1.5:1 to slightly acidic, the available cell capacity based on electrolyte is 160 mA h/g (201 mA h/ml) of electrolyte. Allowing a wider composition variation, such as operating between 1.8:1 to slightly acidic, results in a value of 175 mA h/g (225 mA h/ml) of electrolyte.

Preliminary experiments employing thin-layer electrolysis between Al and carbon rods suggest that the cell is capable of operating over relatively broad composition changes. However, since our cells are positive electrode limited and run in a flooded configuration, the performance limitation imposed by variations in electrolyte composition was not determined in this study.

**Al cyclability.**—Long-term Al cyclability is critical to the cycle life of an Al/Cl<sub>2</sub> secondary cell. High cycling efficiencies have been reported for Al electrodeposition and dissolution in room temperature chloroaluminate (2, 18), indicating the feasibility of Al as a battery electrode in these electrolytes (19). Chronopotentiometric studies in acidic AlCl<sub>3</sub>:DMPPrCl melts show high coulombic efficiencies for Al deposition and stripping (9).

A cycling study was performed to investigate the efficiency of an Al electrode under battery operating conditions. The experiment was designed to simulate deep discharge conditions and to obtain a high degree of Al turnover in an accelerated fashion. A tungsten and an Al electrode were placed in a rectangular cell containing 2 ml of 1.8:1 AlCl<sub>3</sub>:DMPPrCl and the W electrode plates with Al for 6h at 0.5 mA cm<sup>-2</sup>. The plated W electrode was then al-

ternately stripped and plated for 3h intervals at  $\pm 0.5 \text{ mA cm}^{-2}$ .

Cell failure occurred after 195 cycles due to an open-circuit condition. Examination revealed that failure had occurred at the Al electrode, which had corroded through at the top and had thickened at the bottom. We believe this is due to uneven deposition and dissolution rates for Al as a result of the more dense acidic electrolyte settling near the bottom of the cell during Al oxidation. However, the lack of polarization at the tungsten electrode and the high number of cycles obtained under "deep discharge" conditions for the plated Al show that high cycling efficiency for plated Al is obtained with no apparent electrolyte degradation.

Later studies suggested that a 1.5:1  $\text{AlCl}_3\text{:DMPriCl}$  electrolyte would provide the best conditions for a reversible Al electrode. This was confirmed in the more detailed study of Auburn and Barberio for  $\text{AlCl}_3\text{:MEICl}$  molten salts (2). Therefore, a 1.5:1  $\text{AlCl}_3\text{:DMPriCl}$  electrolyte was employed for the bulk of the Al/Cl<sub>2</sub> cell studies.

**Al/Cl<sub>2</sub> cell performance.**—Al/Cl<sub>2</sub> cells employing graphite intercalation electrodes were cycled under a range of conditions to characterize cell performance, as described in the Experimental section. A typical charge/discharge curve generated under computer cycling is shown in Fig. 2 for a cell charged to 50% capacity. The charging curve shows a gradually sloped voltage that at the fully charged state approaches a leveling off at 2.3-2.4V. On discharge, a gradually sloped voltage with an average discharge voltage of ca. 1.7V is observed. This gradually sloped discharge is followed by a relatively steep "knee" near full discharge. A series of discharge curves at various current levels is shown in Fig. 3. Although the cell voltage becomes more sloped at high currents, the average discharge voltage and cell capacity remain nearly constant.

The cell capacity is limited by the storage capacity of graphite for chlorine. The fully intercalated graphite-chlorine compound has a composition of  $\text{C}_8\text{Cl}$  (20), corresponding to 279 mA h/g graphite. However, this compound is stable only at low temperature. Hence, at 150°C, only a residual amount of chlorine corresponding to  $\text{C}_{80}\text{Cl}$  (i.e., 28 mA h/g) remains (17). For our cells at 20°-25°C, we typically obtain capacities in the range of 35-40 mA h/g graphite (~64W h/kg) corresponding to a graphite intercalation compound of ~ $\text{C}_{60}\text{Cl}$ . Cell capacity generally increases for the first several cycles. While some chlorine may be initially retained as a graphite chloride residual compound, this is most likely minor. More importantly, we believe, is that the initial intercalation/deintercalation cycles cause a swelling of the bonded graphite electrode, providing increased accessibility to the active material. After these early cycles, the capacity remains nearly constant over most of the cycle history. Cell failure is characterized by a relatively sharp drop in capacity. This is illustrated in Fig. 4 for a cell under accelerated life test employing a 10% overcharge and high cycling currents.

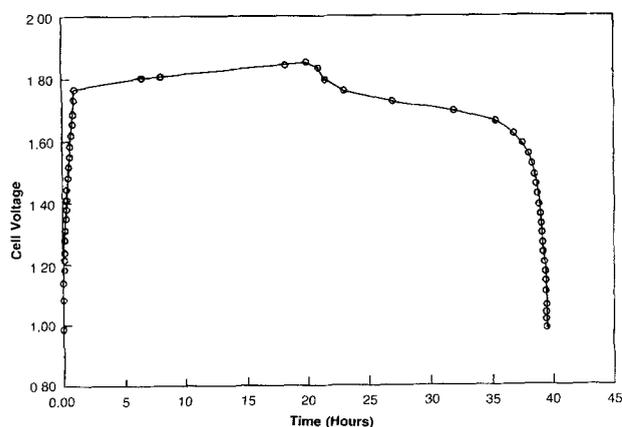


Fig. 2. Charge/discharge curve for Al/Cl<sub>2</sub> cell, cycle no. 125. Charge current = discharge current = 1 mA/g, charge time = 20h.

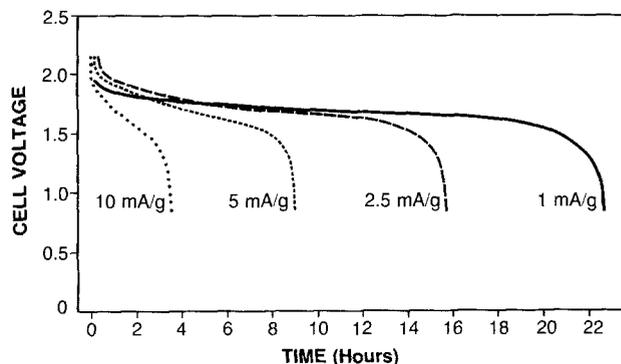


Fig. 3. Discharge curves for Al/Cl<sub>2</sub> cell at various discharge currents

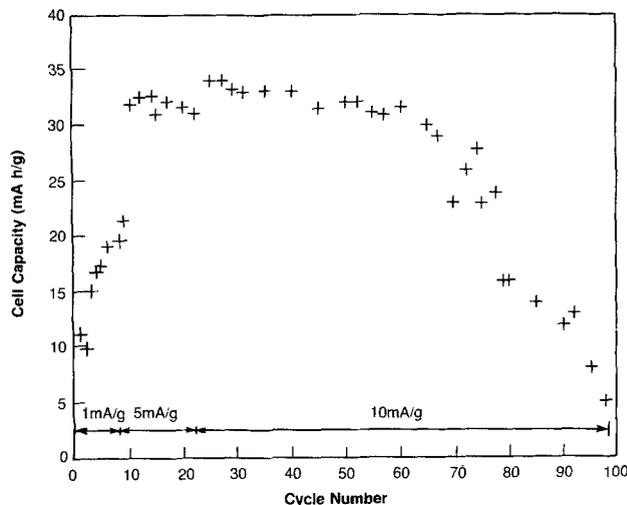


Fig. 4. Cell capacity vs. cycle number for Al/Cl<sub>2</sub> cell under accelerated test conditions.

Cells have been successfully cycled under varying conditions from full capacity to 100% DOD in excess of 150 cycles with the best performance to date being 195 cycles. Cell failure is due to disintegration of the graphite electrode, apparently due to volume changes during the intercalation/deintercalation processes.

Coulombic efficiency ( $Q_{\text{discharge}}/Q_{\text{charge}}$ ) is 80-90% after electrode break-in. The less than 100% efficiency is apparently not caused by detrimental side reactions as it remains constant over the cycling history. It is most likely due to some parallel self-discharge and some free Cl<sub>2</sub> production. Cells could tolerate a degree of overcharge, however, prolonged overcharge accelerated cell failure.

Cells were left in open circuit after charging to determine self-discharge behavior. Cells show an initially high self-discharge rate, losing 20-25% capacity after several days. This rate then decreases and after a period of several weeks at open circuit, cells retain greater than 50% capacity. We believe the principal cause of self-discharge is diffusion of Cl<sub>2</sub> from the graphite electrode. The change in self-discharge rate may indicate that some chlorine is only weakly intercalated or even only surface adsorbed, while in the lower stage graphite chloride compound, the chlorine is more strongly held and hence not readily lost on open circuit.

The effect of temperature on cell performance was briefly investigated over the range of 5°-110°C. Cell performance shows little variation over the range of 5°-80°C. There is a slight increase in cell discharge voltage with increased temperature, probably due to electrolyte resistance effects. A slight drop in capacity is observed with increasing temperature up to 80°C, after which the capacity decreases rapidly with further increase in temperature. This may be due to an increase in the self-discharge rate or instability of the graphite chloride intercalation compound at higher temperatures.

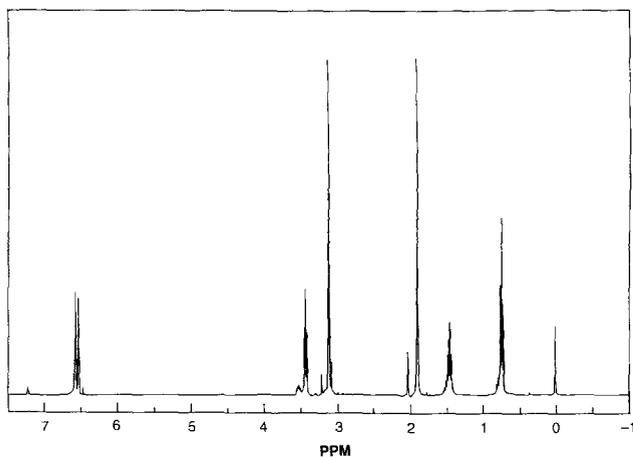


Fig. 5. Proton NMR spectrum of cell electrolyte after exhaustive cycling.

**Electrolyte stability.**—It has been shown that for acidic  $\text{AlCl}_3\text{:MEICl}$  molten salts, chlorine introduced as  $\text{Cl}_{2(g)}$  reacts with the organic cation to form 4,5-dichloro-1-methyl-3-ethylimidazolium ion, suggesting that these electrolytes would not be suitable for use in conjunction with a chlorine electrode (21). An investigation was carried out to determine if a similar reaction was occurring during cycling of our  $\text{Al/Cl}_2$  cells, resulting in chlorination of the imidazolium ion.

A sample of battery electrolyte was obtained from a cell that was cycled until failure at  $\pm 10$  mA/g with a deliberate 10% overcharge. These were considered extreme conditions most likely to lead to free  $\text{Cl}_2$  evolution and/or chlorination of the melt. The total charge passed was more than twice that necessary to chlorinate all of the imidazolium ion present. This sample was then analyzed by proton and  $^{13}\text{C}$  NMR as described in the Experimental section.

The proton NMR spectrum (Fig. 5) is nearly identical to the spectrum observed for the  $\text{DMPriCl}$  salt dissolved in

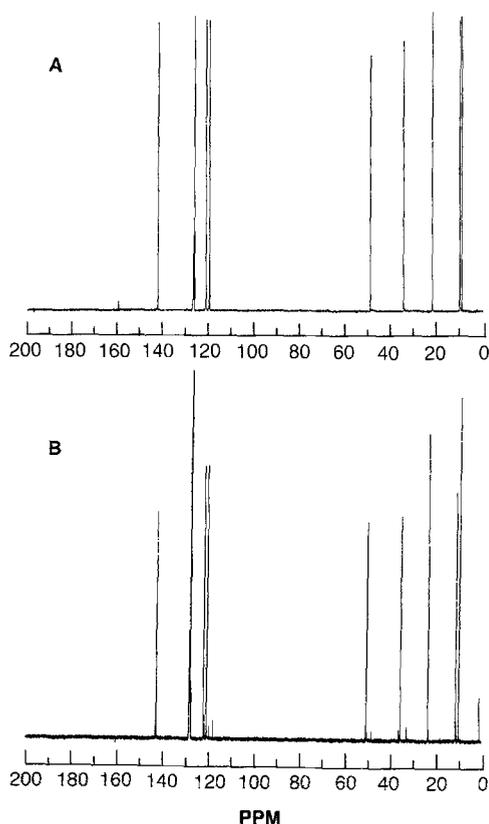


Fig. 6.  $^{13}\text{C}$  spectra of cell electrolyte before (A) and after (B) exhaustive cycling.

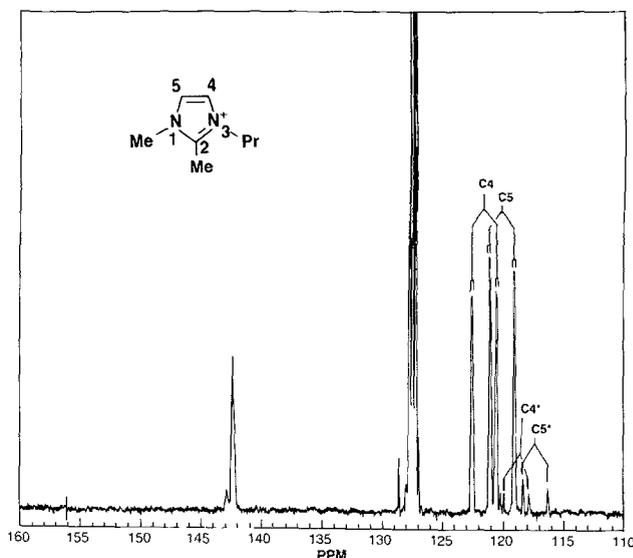
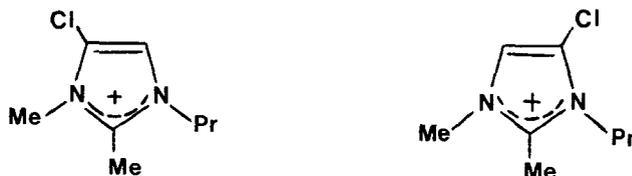


Fig. 7. Proton-coupled  $^{13}\text{C}$  spectrum showing aromatic region for cell electrolyte after exhaustive cycling.

$\text{CD}_3\text{OD}$ . The ring protons are observed as a doublet at 6.5 ppm, suggesting no chlorination. However, there are several small anomalous peaks observed, most notably at 6.4 and 7.2 ppm, that could be due to an impurity or a small amount of chlorinated melt. Therefore, the proton NMR was considered insufficient evidence and  $^{13}\text{C}$  NMR spectroscopy was employed in an effort to better identify the possible species giving rise to these peaks.

The proton-decoupled  $^{13}\text{C}$  NMR spectra are shown in Fig. 6 for fresh melt (A) and spent battery electrolyte (B). Comparing A and B, a number of small peaks are observed in the electrolyte spectrum which are not present in the spectrum of the original melt and must therefore arise from species formed during cell cycling. The spectrum for the cycled electrolyte was studied more closely in the aromatic region with proton-coupled NMR (Fig. 7). The strong doublets centered at 120.1 and 121.6 are due to the C4 and C5 ring carbons. (The strong peak at 127.5 is due to  $\text{C}_6\text{D}_6$ .) The appearance of these peaks as split doublets clearly shows that both the resonant carbon and the adjacent carbon have attached protons and therefore are not chlorinated. However, the minor peaks show up as simple doublets. This shows that the resonant carbon has an attached proton and that the adjacent carbon does not. Based on this evidence, we attribute these minor peaks as due to two monochloro species



From intensities of these minor peaks in a suppressed nuclear Overhauser experiment, we conclude that these species are present at about the 10 mol percent level or less. Therefore, it would appear that chlorination of the melt is not a serious problem in a battery employing an intercalation cathode for chlorine under normal cycling conditions.

### Conclusions

A reversible electrochemical cell employing an Al negative electrode and graphite positive electrode in a room temperature molten salt has been successfully demonstrated. The graphite electrode functions as a reversible intercalation electrode for chlorine. Use of an intercalation electrode for chlorine provides for a reversible chlorine electrode in an acidic melt while apparently preventing chlorination of the melt, permitting the cell to operate in a

melt of single composition. The cell shows good cyclability and voltage properties for a secondary battery. However, the storage capacity of graphite for chlorine is too low to achieve suitable energy densities and higher capacity chlorine electrodes are needed for a practical battery system. The need to accommodate compositional changes in the electrolyte also places a limit on the cell energy density. Further work with scaled up and optimized cells would be required to determine practical volumetric and gravimetric energy densities.

#### Acknowledgments

The authors thank Dr. L. Shacklette for helpful discussions and Dr. T. Palanisamy for his contributions on computer software for cell cycling. The authors also thank Dr. R. Brambilla for his contributions in obtaining and interpreting the  $^{13}\text{C}$  NMR results. Portions of this work were presented at the EuChem Conference on Molten Salts, Geiranger, Norway, August 1986.

Manuscript submitted Feb. 5, 1987; revised manuscript received July 24, 1987.

Allied-Signal Incorporated assisted in meeting the publication costs of this article.

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## Technical Notes



### Selected Transport Properties of Some Electroless Copper Plating Baths

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Mass transport of cupric ions has been shown to play a significant role in the electroless copper plating process (1, 2). In the past, diffusivities of transporting species and other transport properties of the baths had to be estimated using traditional methods (1, 2). Certain transport properties are required for a complete analysis of mass transport effects *per se* (1, 2) and their effects on the kinetics of electroless copper plating processes (2). Since these transport properties are not available in the literature, it was decided to measure the kinematic viscosities and densities of selected electroless copper plating baths and the diffusion coefficients,  $D$  ( $\text{cm}^2/\text{s}$ ), of some cupric ion complexes in these baths. In order to provide parameters which can be useful to other investigators, correlation equations relating

dynamic viscosity and density to bath composition and temperature and computed values of the quantity  $D\rho/T$  ( $\text{g-cm}^3/\text{K-s}^2$ ) will be presented.

The bath compositions were similar to those studied earlier (3-5). The ligands used in the kinematic viscosity and density measurements were EDTA, Quadrol [N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine], and tartrate. A Cannon-Fenske viscometer was used to determine the kinematic viscosities at 30°, 40°, and 50°C with double-distilled water as the reference fluid. The densities of the baths were determined with a hydrometer. The dynamic viscosities were computed from the quotient of the measured kinematic viscosities and densities. The diffusivities of the copper ion complexes were determined from cathodic (metal deposition) limiting current density—rotation rate measurements at rotating disk (for EDTA solutions) and cylinder (for Quadrol solutions) electrodes.

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