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Investigation of the 1-methyl-3-ethylimidazolium chloride–$AlCl_3$/$LiAlCl_4$ system for lithium battery application

Part I: Physical properties and preliminary chronopotentiometric study

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The applicability of the 1-methyl-3-ethylimidazolium chloride – $AlCl_3$ system for lithium battery application was investigated. Lithium chloride was found to dissolve up to 1.59 mole ratio of $LiAlCl_4$/$MeEtImAlCl_4$ upon reaction between LiCl and $AlCl_3$ in the melt. Density, conductivity and viscosity of the melt upon addition of $LiAlCl_4$ were determined. The density was found to increase monotonically from 1280 to 1480 kg m^{-3}, while the conductivity decreased rapidly from the initial value of 5.6 mS to a steady plateau at 3.4 mS. The viscosity was varied from 1.46 Ns m^{-2} to a small but distinct initial fall prior to rising to 2.75 Ns m^{-2} when the mole ratio of $LiAlCl_4$ increased from zero to 1.59. The chronopotentiometric studies indicate a satisfactory electrochemical behaviour with no apparent attack of the melt by the formation of the reactive lithium alloys. 350 cycles were achieved with cycling efficiency over 90% using an optimal c.d. of 6 mA cm^{-2} for lithium deposition on aluminium substrate in the melt. Prolonged cycling improved the nucleation rate but led to an increase in the internal resistance and a gradual reduction in the charge and discharge capacity.

1. Introduction

One of the major problems facing the development of the secondary lithium battery is the reactivity of the lithium anode towards the solvent, in particular with the use of organic solvents [1]. The use of high temperature molten salt as the reaction medium gave satisfactory cycling life but suffered the disadvantage of the necessity of insulation and heat management during operation of the battery. The development of the room temperature molten salt system based on the 1-methyl-3-ethyl-imidazolium chloride aluminium chloride ($MeEtImAlCl_4$) melt [2–4] provides a promising system due to its inertness towards lithium and the capability of operation at room temperature.

Although the MeEtImCl–$AlCl_3$ system has been studied for application in the cadmium–bromine rechargeable battery [5], it has not been used for the more reactive and higher energy lithium system. The reasons for this are the lack of physical data for evaluation, in particular the solubility and conductivity data for lithium rich MeEtImCl–$AlCl_3$ melts, the availability of suitable reactive anode and cathode materials and information on their electrochemical behaviour under different melt compositions.

In view of the above problems, the physical properties and electrochemical behaviour of the melt under different lithium compositions have been investigated. The structure of the melt has also been studied using infrared and NMR techniques and the melt composition correlated with their electrochemical behaviour under cyclic voltammetry and chronopotentiometry. This paper reports on the physical properties of the melt and gives preliminary results on the cycling studies to illustrate that this system is a suitable candidate for lithium battery application.

2. Experimental details

2.1. *Chemicals and material*

The synthesis of 1-methyl-3-ethylimidazolium chloride by direct reaction between 1-methylimidazole (Aldrich) with ethyl chloride (BDH) under elevated pressure has been described elsewhere [6]. Aluminium chloride (Fluka) was purified by sublimation under vacuum in the presence of a bundle of aluminium wires (BDH) and a little sodium chloride (BDH). Lithium chloride (BDH) was vacuum dried at a temperature slightly over 100 °C for 24 h before use. The preparation of the melt and solution were performed inside a glove box with positive pressure under argon.

2.2. *Physical properties measurement*

The specific conductivities of various melt compositions were measured at 24 °C using a Radiometer Conductivity meter type CDM 2C calibrated against

0.1 M aqueous KCl standard. A closed and submersible all Pyrex viscometer [6] was used for viscosity measurement. The viscometer was calibrated at different temperatures using cyclohexanol and ethylene glycol. Densities were measured using a 1.00 cm^3 Pyrex pipette (DESAGA) and its volume was calibrated against distilled water gravimetrically. The volume of this type of pipette was $1 \pm 0.006\ cm^3$ and all weighings were done using an electronic balance (Mettler, model AE101) inside a glove box.

For the solubility studies, equimolar $AlCl_3$ and LiCl were weighed to about 2 g and mixed together. The neutral binary melt was then added drop by drop to the mixture under stirring until a clear solution was formed. The melt temperature was kept at 24.1 °C. A Varian 575 atomic absorption spectrometer was used to analyse the lithium content in the lithium chloride saturated melt using the flame atomic emission method. The lithium content was counter checked using the gravimetric method.

2.3. *Electrode preparation and electrochemical apparatus*

An Al/Al^{3+} system (aluminium wire immersed in acidic melt with mole ratios of $AlCl_3$: MeEtImCl = 1.5 : 1) was used as the reference electrode throughout the study. The counter electrode was a lithium wire inserted in the melt with immersed surface area approximately 2 cm^2. An aluminium wire of 0.76 mm in diameter was used as the working electrode and it was cleaned and degreased with acetone prior to immersion in an acid mixture (HNO_3 : H_2SO_4 : H_3PO_4 = 30 : 30 : 40, v/v) to remove the surface oxide layer. It was then washed with deionized water and dried in a vacuum oven prior to use. The electrode was inserted in the melt to a given mark for a depth of 0.7 cm in order to maintain a constant electrode surface area for cycling studies. The nickel electrode was obtained by sealing a nickel wire in a heat shrinkage plastic tubing with an exposed area of 6 mm^2. It was cleaned with acetone, acid and deionised water by the same procedure as the aluminium electrode prior to drying before use.

For electrochemical studies, a PAR model 363 potentiostat/galvanostat was used to provide a constant current for chronopotentiometric studies. The voltage output was recorded using a Linesis *Y–t* chart recorder. For the galvanostatic cycling studies, a self-constructed electronic automatic switching unit was used to switch the current at preset potential limits (both cathodic and anodic) between the reference electrode and the working electrode. The current step signal was generated by a Chemical Electronics model 01 waveform generator.

3. Results and discussion

3.1. *Solubility of LiCl in* $MeEtImAlCl_4$

One of the major problems facing the use of the 1-methyl-3-ethylimidazolium chloride/aluminium chloride system for lithium battery application is the apparent lack of solubility of lithium salts. This problem had been solved [4, 7, 8] by first adding a given amount of $AlCl_3$ in the neutral melt prior to the addition of LiCl. In effect, this is a chemical reaction in the melt as indicated by the following equation,

$$LiCl + AlCl_3 \rightarrow LiAlCl_4 \quad (1)$$

Table 1. Solubility of $LiAlCl_4$ *in* $MeEtImAlCl_4$

Method	*Experiment I*		*Experiment II*	
	A	*B*	*A*	*B*
AES	2.82	0.610	2.81	0.608
Gravimetric	2.84	0.614	2.84	0.614

A: Concentrations expressed as mole ($LiAlCl_4$) per kg melt
B: Concentrations expressed as mole fraction of ($LiAlCl_4$)
Temperature: 24 °C

Thus, the solubility of LiCl can be expressed as moles of $LiAlCl_4$ dissolving in neutral melts (mole ratios of MeEtImCl : $AlCl_3$ = 1 : 1). Two methods, the gravimetric method and atomic emission spectrophotometry (AES), were used to determine the solubility of $LiAlCl_4$ in neutral melts and the results are given in Table 1. To facilitate comparison, the data are expressed as both mole fraction and mol kg^{-1} melt. Comparing with the literature value of 0.1 mole fraction of LiCl in basic melt [9, 10], the solubility of lithium chloroaluminate is very much enhanced using the procedure as described above. The much higher solubility of LiCl obtained also indicates that this melt can be used as medium for rechargeable lithium battery application.

3.2. *Density, conductivity and viscosity*

The results for the variation of the density, conductivity and viscosity of the $MeEtImAlCl_4$ melt with different amounts of added $LiAlCl_4$ are given in Fig. 1. Mole ratio is used here to express the results as the formation of the intermediate compounds at progressively higher lithium concentrations can be easily identified when the data are plotted graphically.

The density of the melt is shown to follow a monotonic increasing function of the lithium chloroaluminate content. The increase in density of the chloroaluminate melts was shown to follow the gradual replacement of the lighter chloride ion by the heavier chloroaluminate anion and the formation of dimeric chloroaluminate ions upon increasing acidity of the melt [3, 10]. The case for the increase in density with the addition of $LiAlCl_4$ is different as lithium is a lighter cation compared to the imidazolium ion. This is probably due to the very small size of the lithium ion which enables it to occupy the space between the large cations and anions, thus leading to a higher density upon increasing $LiAlCl_4$ concentration.

The specific conductivity of the melt was found to

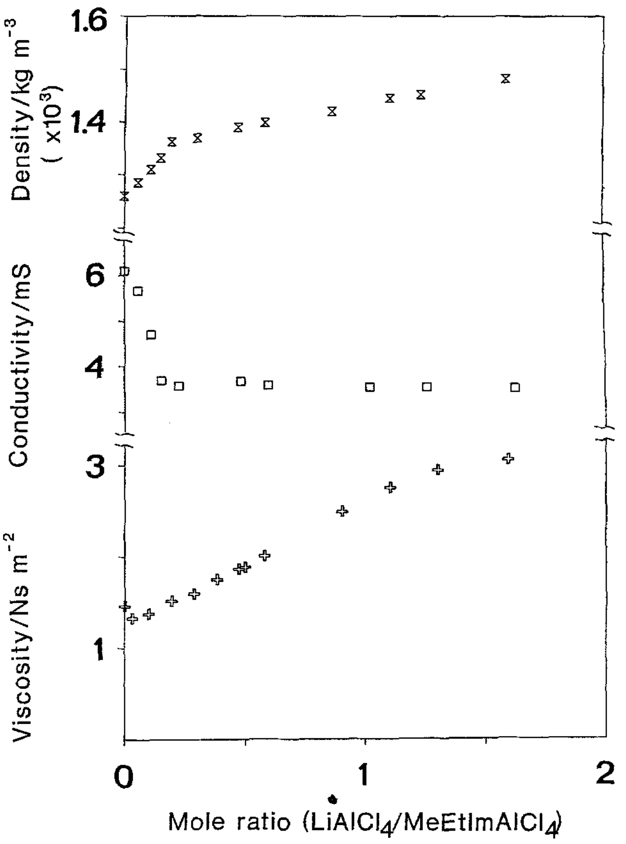

Fig. 1 . Density, conductivity and viscosity of MeEtImAlCl$_4$ melt at different mole ratios of LiAlCl$_4$. The zero mole ratio data for density and conductivity were taken from [11].

fall rapidly when a small amount of LiAlCl$_4$ was added and it was stabilized when the mole ratio was greater than 0.15. The initial reduction in conductivity may be due to the large polarization effect on nearby AlCl$_4^-$ anions by the Li$^+$ as a result of its small size. Thus, ion association would occur which slows down the movement of the chloroaluminate anion producing a drastic reduction in the specific conductivity upon addition of a small amount of LiAlCl$_4$. Further addition of Li$^+$ would lead to two opposing effects. Due to the small size of lithium, the number of ions per unit volume is increased as lithium ions can occupy the space between the large cations such as MeEtIm$^+$ and the anion AlCl$_4^-$. This leads to the increase in density of the melt at high lithium mole ratios as described above and hence the increase in the specific conductivity when more lithium ions are added. However, on the other hand, the polarization effect of lithium and the formation of ion pairs or other forms of association lowers the conductivity. The occurrence of two more or less balancing opposite forces leads to the stabilisation of the specific conductivities at higher mole ratios of LiAlCl$_4$ in the melt. This is illustrated more clearly by plotting the molar conductivity against mole ratio as shown in Fig. 2.

The kinematic viscosity, v, of the melt, determined using the closed viscometer, was calculated using the following equation [11].

$$v = At + B/t \qquad (2)$$

where A and B are constants (0.1306 and 9.884, respectively, by experimental calibration), and t is the efflux time in seconds.

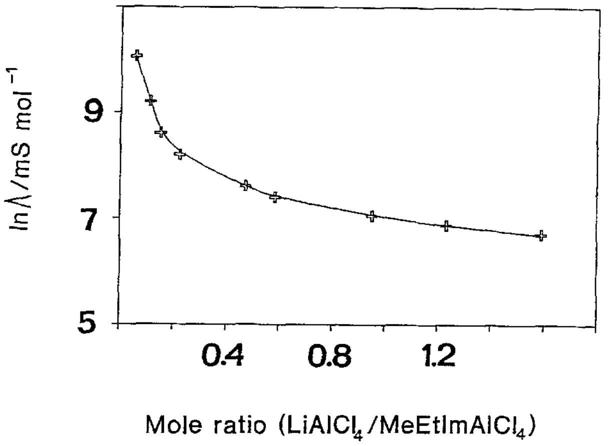

Fig. 2. The variation of molar conductivity at different mole ratios of LiAlCl$_4$.

A small but distinct and repeatable fall in the kinematic viscosity was observed upon addition of a small amount of LiAlCl$_4$ (Fig. 1) and it increased with increasing mole ratio of LiAlCl$_4$. The change in the neutral melt structure upon addition of lithium may be responsible for the small initial fall. Further addition of lithium may lead to a more closely packed structure, and hence increasing viscosity, at high lithium mole ratios.

The absolute viscosity, η, can be calculated as

$$\eta = \rho v \qquad (3)$$

where ρ is the density of the melt.

To test whether or not the absolute viscosity exhibits Arrhenius temperature dependence, the following equation was used:

$$\eta = \eta_0 \exp(E_a/RT) \qquad (4)$$

where η_0 is the viscosity of pure solvent, R the gas constant, E_a the activation energy, and T the temperature (kelvin).

The graph of ln η was plotted against $1/T$ and the results are shown in Fig. 3. The occurrence of a straight line gives the following relationship:

$$\ln \eta = \ln \eta_0 + E_a/RT \qquad (5)$$

Activation energy, from the slope of the graph, was

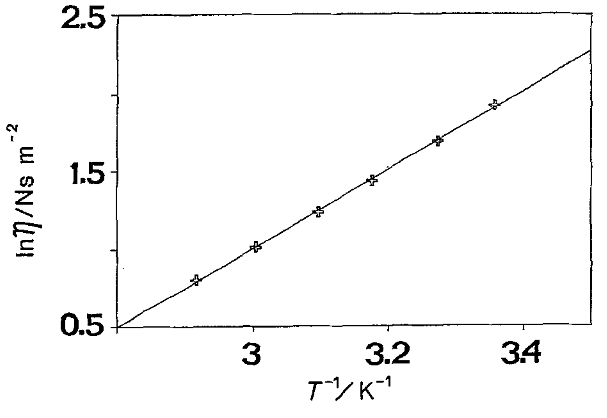

Fig. 3. The temperature effect of the absolute viscosity.

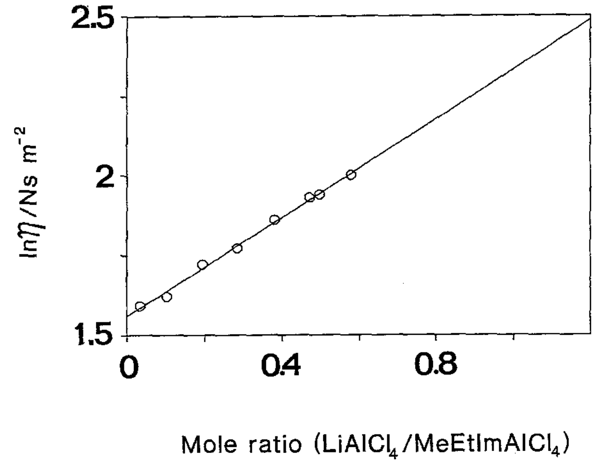

Fig. 4. The variation of the absolute viscosity at different mole ratios of LiAlCl$_4$.

calculated to be 4.85, 4.95 and 5.37 kcal mol^{-1} for mole ratio (LiAlCl$_4$/MeEtImAlCl$_4$) of 0.193, 0.468 and 1.59, respectively. The relatively constant values of the activation energy at mole ratios of 0.193 and 0.468 indicate that there is no abrupt change in the structure of the melt within these mole ratio ranges. However, the change in the activation energy is more noticeable when the mole ratio is increased to 1.59.

A straight line was obtained when ln η was plotted against the mole ratio (Fig. 4) and this agrees with the conclusion drawn from the activation energy study that there is no major change in the structure of the melt at low lithium ratios, as indicated by the change in the physical properties.

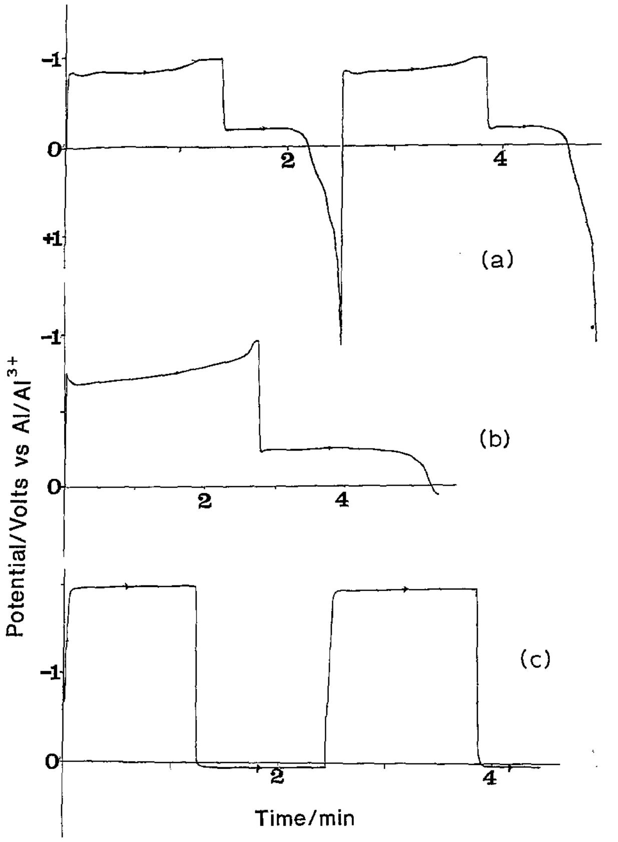

Fig. 5. The chronopotentiograms of neutral melts. (a) Ni working electrode, [LiAlCl$_4$] = 0.84 mol kg^{-1}; (b) Al working electrode, [LiAlCl$_4$] = 0.84 mol kg^{-1}; (c) Al working electrode, no LiAlCl$_4$ added. C.d. = 6 mA cm^{-2}.

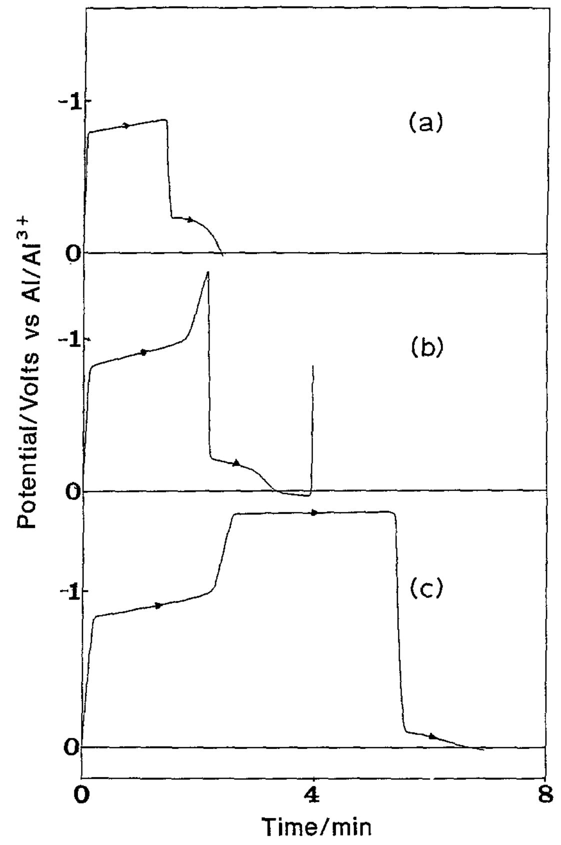

Fig. 6. The effect of cathodic switching potentials on lithium deposition. [LiAlCl$_4$] = 0.84 mol kg^{-1}, (a) −0.88, (b) −1.43 and (c) −1.5 V against Al/Al^{3+}. C.d. = 6 mA cm^{-2}.

In general, the physical properties of the chloroaluminate melt show a noticeable change upon initial addition of LiAlCl$_4$ to the neutral melt, possibly due to the modification of the structure of the melt. However,

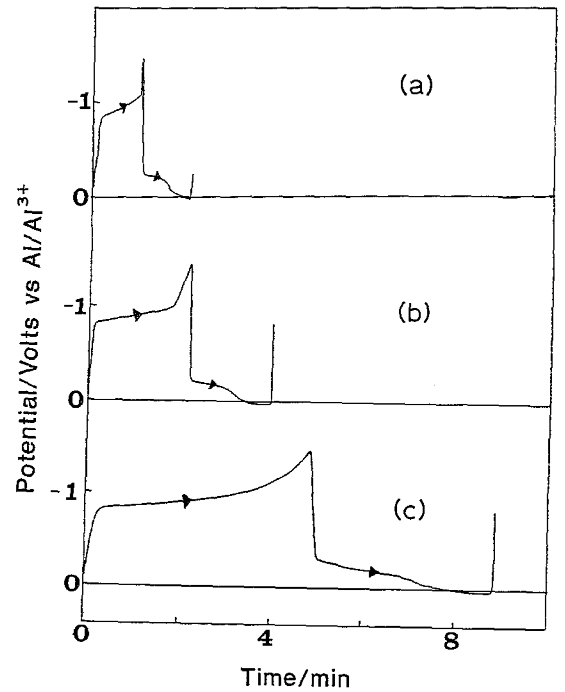

Fig. 7. The chronopotentiograms at different current densities. [LiAlCl$_4$] = 0.85 mol kg^{-1}, (a) 10, (b) 6 and (c) 3 mA cm^{-2}.

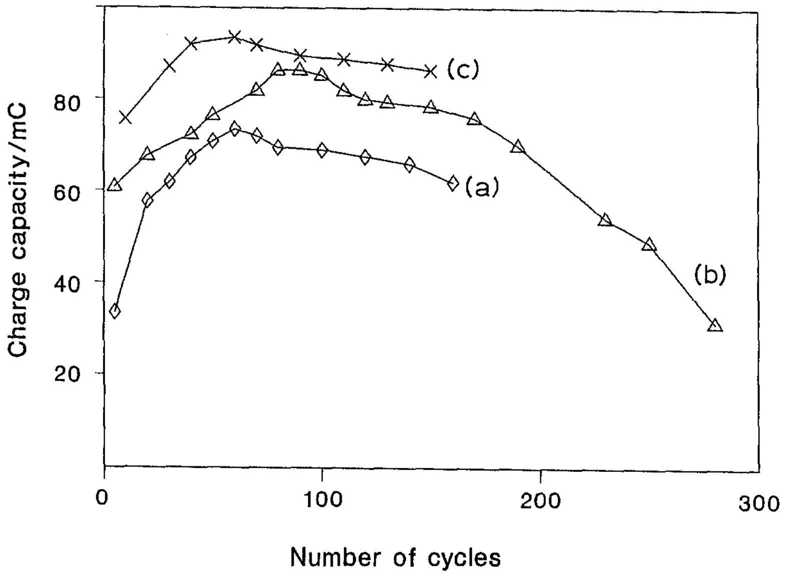

Fig. 8. Charge capacity at different current densities upon cycling. [$LiAlCl_4$] = 0.85 mol kg^{-1}. (a) 10, (b) 6 and (c) 3 mA cm^{-2}.

no major change was observed in the melt upon further addition of $LiAlCl_4$ at low lithium mole ratios, though a noticeable change in the activation energy was observed at melts with high lithium content.

3.3. *Cycling studies*

The cyclic chronopotentiograms of the neutral melt using nickel and aluminium working electrodes are shown in Fig. 5. The chronopotentiograms are well characterized by solvent decomposition at both ends of the potential limits. The chronopotentiograms for a lithium rich neutral melt is shown in Fig. 5(a) and Fig. 5(b) and (c) for the unalloyed substrate (nickel) and alloying substrate (aluminium), respectively. The unalloyed substrate shows no nucleation effect upon electrodeposition of lithium, whereas the aluminium substrate gives a clear potential spike upon current switching (Fig. 5b).

Extending the cathodic limit to the deposition of reactive lithium alloys (Fig. 6) leads to a rapid drop in the coulombic efficiency. However, the chronopotentiogram remains stable with no visual attack of the reactive lithium alloy on the solvent and the same stripping plateaux are observed as compared to those not exposed to the reactive lithium metal.

The use of different current densities (c.d.s) from 3 to 6 mA cm^{-2} does not affect the shape of the chronopotentiograms (Fig. 7). However, it does affect the charge capacity (Fig. 8) and the cycling efficiency (Fig. 9). The charge capacity was calculated as the total charge delivered to the electrode during the formation of the lithium alloys and the cycling efficiency was obtained based on the fraction of charges recovered during the stripping of lithium from the working electrode. It is interesting to note that the best cycling efficiency obtained is using a c.d. of 6 mA cm^{-2} which gave over 90% coulombic efficiency over about 300 cycles. Much lower cycling efficiency was obtained

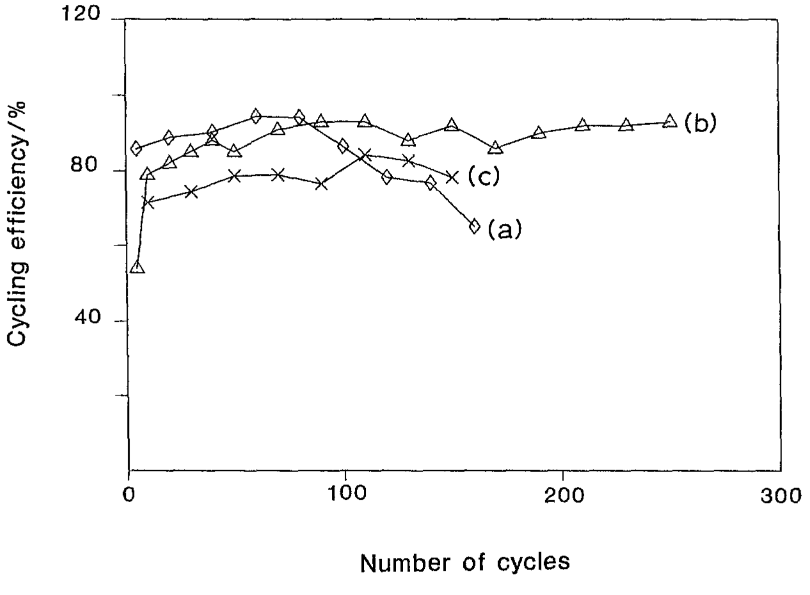

Fig. 9. The variation of cycling efficiency at different current densities upon cycling. [$LiAlCl_4$] = 0.85 mol kg^{-1}. (a) 10, (b) 6 and (c) 3 mA cm^{-2}.

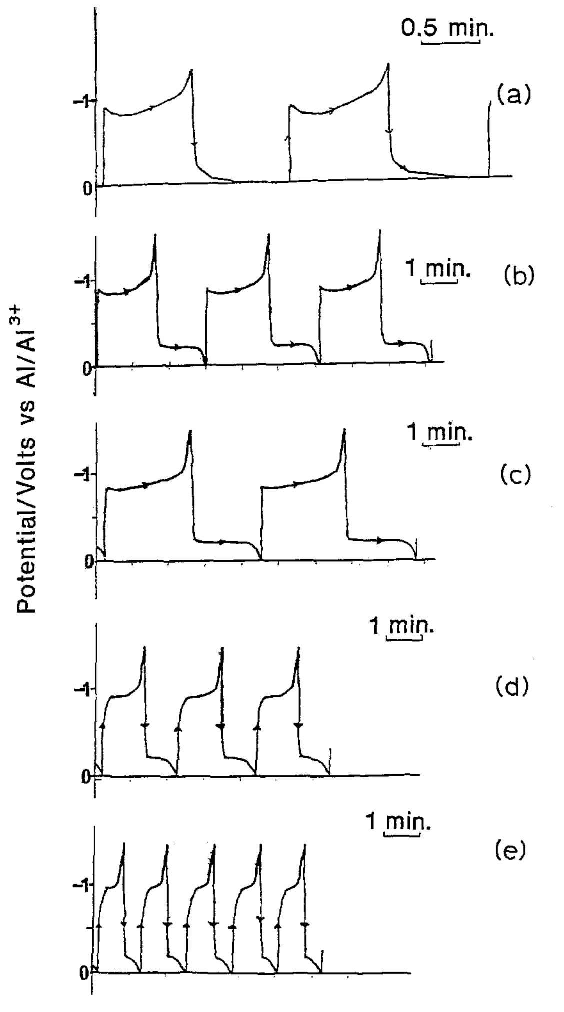

Fig. 10. The change in the chronopotentiograms upon cycling. [LiAlCl$_4$] = 0.85 mol kg^{-1}. Number of cycles: (a) 1st to 2nd (b) 53rd to 55th, (c) 130th to 131st, (d) 230th to 232nd, and (e) 280th to 284th.

in the first cycle due to the build up of lithium during the development of the LiAl electrode (Figs 9 and 10). Charging at high c.d. (10 mA cm^{-2}) gave a lower charge capacity but good cycling efficiency at the first 80 cycles. This may be due to the corrosion effect of impurities as higher c.d. required less time for each cycle.

From the change in the chronopotentiograms upon cycling (Fig. 10), the following observations are made. First, the nucleation effect, as evidenced by the potential spike during the initial lithium deposition, disappears after about 100–130 cycles. Secondly, the potential difference between the charging and discharging plateaux (the α/β LiAl transition) decreases initially and then increases progressively upon cycling. This indicates that resistance was built up in the system upon cycling. Thirdly, both the charging and discharging capacity decrease upon cycling, even though the cycling efficiency remains more or less the same (Fig. 9) upon cycling.

4. Conclusions

The following conclusions can be drawn:

(i) The 1-methyl-3-ethylimidazolium chloride – AlCl$_3$ melt system provides a promising medium for lithium battery application.

(ii) A procedure employing chemical reaction between AlCl$_3$ and LiCl in the MeEtImAlCl$_4$ melt was found to enhance the solubility of LiCl.

(iii) Up to 1.6 mole ratio of LiAlCl$_4$ in MeEtImAlCl$_4$ can be obtained using the above procedure and this provides sufficient amounts of lithium in the melt for lithium battery application.

(iv) Density, conductivity and viscosity of the MeEtImAlCl$_4$ melt were determined at different concentrations of LiAlCl$_4$. The conductivity and the viscosity of the melt gave an abrupt change when small amount of lithium was added, possibly due to the effect of changing the structure of the neutral melt upon addition of lithium ions. No major change was detected in the melt upon further addition of lithium as revealed by the change in the physical properties when the mole ratios of lithium is low in the melt.

(v) Upon addition of LiAlCl$_4$, the density was found to increase and the conductivity to decrease till a steady state was reached at a mole ratio of 0.15. However, the viscosity was found to increase with increasing LiAlCl$_4$ concentration after an initial fall. All these changes are in a direction unfavourable for lithium battery application, although they are within reasonable limits.

(vi) The preliminary cycling studies indicate a satisfactory capacity and cycling life using aluminium as the substrate. No evidence of attack of the reactive lithium alloy on the melt is obtained during the study.

(vii) Up to a cycling number of 350 was obtained with cycling efficiency of over 90% using an optimal c.d. of 6 mA cm^{-2} for cycling. The deterioration upon cycling led to the increase in the internal resistance and a gradual reduction on the charge and discharge capacity. However, improvement has been observed for the rate of nucleation of the lithium alloy on aluminium upon cycling.

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