PRIMARY AND SECONDARY ROOM TEMPERATURE MOLTEN SALT ELECTROCHEMICAL CELLS

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Summary

Three primary cells (a, b, and c) and two secondary cell candidates (d and e) were examined in room temperature molten salt electrolytes containing either 1-methyl-3-ethylimidazolium chloride (MEICl) (a, b, d, and e), or 1-methyl-3-ethylimidazolium bromide (MEIBr) (c).

(a) Al anode/$AlCl_3$–MEICl ($N = 0.37$)//$FeCl_3$–MEICl ($N = 0.33$)/W cathode

(b) Al anode/$AlCl_3$–MEICl ($N = 0.37$)//WCl_6–MEICl ($N = 0.33$)/W cathode

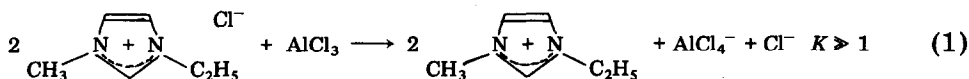(c) Al anode/$AlBr_3$–MEIBr ($N = 0.33$)/Br_2/RVC, Pt cathode

(d) Zn anode/$AlCl_3$–MEICl ($N = 0.33$)//$AlCl_3$–MEICl ($N = 0.60$)/Al cathode

(e) Cd anode/$AlCl_3$–MEICl ($N = 0.33$)//$AlCl_3$–MEICl ($N = 0.60$)/Al cathode

where N is the mole fraction of aluminium halide in the melt. An IONAC® anion exchange membrane separated the anolyte and catholyte solutions in cells (a) and (b), while in cells (d) and (e) a NAFION® cation exchange membrane separated the anolyte and catholyte solutions. In cell (c) a phase boundary separated the anolyte and catholyte solutions, with reticulated vitreous carbon (RVC) acting as the anode current carrier.

Introduction

Previous work in this laboratory [1] has shown that when aluminum chloride is added to 1-methyl-3-ethylimidazolium chloride, a room temperature molten salt is formed which initially consists of the tetrachloroaluminate anion, imidazolium cation, and chloride anion, as shown in eqn. (1):

$$2 \underset{CH_3}{\overset{Cl^-}{\boxed{N + N}}}_{C_2H_5} + AlCl_3 \longrightarrow 2 \underset{CH_3}{\boxed{N + N}}_{C_2H_5} + AlCl_4^- + Cl^- \quad K \gg 1 \quad (1)$$

The above equation depicts the case in which the mole fraction, N, of $AlCl_3$ in the molten salt is 0.33. When N is less than 0.5, the solution is

referred to as basic, due to the presence of the Lewis base, Cl^-. When N is between 0.5 and 0.67, the solution is referred to as acidic, due to the presence of the Lewis acid $Al_2Cl_7^-$, as shown in eqn. (2):

$$AlCl_4^- + AlCl_3 \longrightarrow Al_2Cl_7^-, \qquad\qquad K \geqslant 1 \qquad\qquad (2)$$

It has also been shown [2] that a battery using separated basic anolyte and acidic catholyte melts with aluminum electrodes exhibits an open-circuit voltage of 1.38 V. The reactions are:

$$\text{anode: } Al + 4Cl^- \longrightarrow AlCl_4^- + 3e^- \qquad\qquad (3)$$

$$\text{cathode: } 4Al_2Cl_7^- + 3e^- \longrightarrow Al + 7AlCl_4^- \qquad\qquad (4)$$

$$\text{cell: } Al + 4Al_2Cl_7^- + 4Cl^- \longrightarrow Al + 8AlCl_4^- \qquad\qquad (5)$$

The theoretical specific energy of the electroactive materials in a cell based on reaction (5) is 82 W h/kg. This specific energy will be compared with the theoretical specific energy of some of the cells described in this research.

A previous survey of the electrochemistry of metal chlorides dissolved in $AlCl_3$–MEICl molten salts [3] indicated that $FeCl_3$ and WCl_6 offered promise for reducible species at the cathode. In the present study, rather than dissolving these metal halides in $AlCl_3$–MEICl, both $FeCl_3$ and WCl_6 were mixed with 1-methyl-3-ethylimidazolium chloride in 1:2 molar ratio to form the room temperature molten salts $FeCl_3$–MEICl and WCl_6–MEICl, respectively. In the case of cell (c), the $AlCl_3$–MEICl electrolyte was replaced by an $AlBr_3$–MEIBr electrolyte. Our experience indicates that these two electrolytes are chemically similar. Thus, from 0 to 0.5 mole fraction of $AlBr_3$, the anions $AlBr_4^-$ and Br^- are present, and from 0.5 to 0.67 mole fraction of $AlBr_3$, the anions $Al_2Br_7^-$ and $AlBr_4^-$ are present.

Since aluminum cannot be reversibly plated from a basic haloaluminate melt [2], cells such as (a), (b), and (c) are not reversible, since the anode in each case is an aluminum electrode in contact with a basic melt. Cells (d) and (e), however, have the potential for reversibility, since the aluminum electrode is used as the cathode in contact with an acidic melt. Recent work has indicated that aluminum can be plated reversibly from an acidic chloroaluminate melt of around 0.60 mole fraction of $AlCl_3$, with the melt being stable to repeated cycling [4].

Experimental

Anhydrous $FeCl_3$ (99.999%) and anhydrous $CdCl_2$ (99.999%) were obtained from Atomergic Chemetals Corp., and the anhydrous WCl_6 and $ZnCl_2$ from Ventron Products. Aluminum chloride and $AlBr_3$ were purified by sublimation, and the 1-methyl-3-ethylimidazolium halides were synthesized and recrystallized following procedures described elsewhere [1]. All melts were prepared, and all experiments performed under dry helium. The W, Al, and Cd foils and Al wire used for the electrodes were polished with
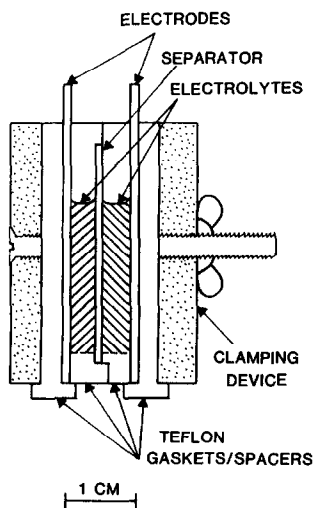
Fig. 1. Configuration for cells (a), (b), (d) and (e).

silicon carbide paper in the dry box before use. With the exception of cell (c), all the cells were constructed by clamping the anode, separator and cathode between Teflon gasket/spacers, as shown in Fig. 1. The electrodes were 0.25 mm thick with about 5 cm^2 of active area, and were about 1 cm apart in the assembled cell. The IONAC® MA3475 anion exchange membrane was obtained from Sybron Chemical Co., and the NAFION® reinforced cation exchange membrane from E. I. DuPont de Nemours & Co. The NAFION® membrane was soaked in acetonitrile solution containing 10% w/w dissolved 1-methyl-3-ethylimidazolium chloride salt before use.

Results and discussion

(i) Cells using IONAC separators

Cell (a)

Al anode/AlCl$_3$–MEICl (N = 0.37)//FeCl$_3$–MEICl (N = 0.33)/W cathode

Mixing pure, anhydrous FeCl$_3$ with 1-methyl-3-ethylimidazolium chloride (MEICl) in a 1:2 molar ratio gave a brownish-colored, room temperature molten salt. The cathode compartment of this cell consisted of a tungsten foil electrode along with the FeCl$_3$–MEICl (N = 0.33) catholyte, while the anode compartment consisted of an aluminum foil electrode and an AlCl$_3$–MEICl (N = 0.37) anolyte.

Initially, this cell gave a stable, open-circuit potential of 1.75 V. In order to investigate the electrode reactions, a 0.1 mA current was allowed to pass for 52.7 h during which time the load voltage dropped slowly from 0.79 to 0.63 V, with the open-circuit potential after discharge being 1.69 V. The aluminum and tungsten electrodes were then removed from the cell, wiped gently, and rinsed with acetonitrile. After drying and weighing in the

dry box, the change in weight of the W electrode (+0.04%) was found to be negligible within experimental error. A previous study [2] of the anode reaction invovling Al immersed in $N = 0.37AlCl_3-MEICl$ melt found the loss in weight of the anode to be consistent with the reaction:

$$Al + 4Cl^- \longrightarrow AlCl_4^- + 3e^- \tag{6}$$

Previous work by Hussey et al. [5, 6] indicated that in a chloride ion-rich molten salt, iron(II) and iron(III) chlorides form the complexes $FeCl_4^-$ and $FeCl_4^{2-}$, respectively. Also, Piersma and Wilkes [3] showed by cyclic voltammetry that the iron(III) chloride complex underwent a reversible one-electron reduction in a basic $AlCl_3-MEICl$ melt. In our case, about 3 mmole of $FeCl_4^-$ was present in the cathode compartment, and about 2 meq. of current was passed. The one-electron cathode reduction can be written:

$$FeCl_4^- + e^- \longrightarrow FeCl_4^{2-} \tag{7}$$

The overall cell reaction is thus:
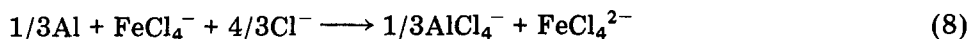
$$1/3Al + FeCl_4^- + 4/3Cl^- \longrightarrow 1/3AlCl_4^- + FeCl_4^{2-} \tag{8}$$

The theoretical specific energy of the electroactive materials in a cell based on reaction (8) is approximately 200 W h/kg.

The same cell as (a) above was studied except that an Fe metal cathode was used as the cathode in place of the W metal cathode. Whereas in the previous case the W cathode weight remained constant, the 2.3923 g Fe cathode suffered a weight loss of 5.7 mg while in the $FeCl_3-MEICl$ melt, and the open-circuit potential of the cell decreased markedly to 1.38 V. This dissolution of a metal in molten salts containing the corresponding metal halide is not unique according to the literature [7]. For example, Cd is known to dissolve in molten $CdCl_2-AlCl_3$ to form $Cd_2^{2+}[AlCl_4^-]_2$.

Cell (b)
Al anode/AlCl$_3$–MEICl (N = 0.37)//WCl$_6$–MEICl (N = 0.33)/W cathode

Mixing WCl_6 with 1-methyl-3-ethylimidazolium chloride in a 1:2 molar ratio gave a viscous, brown, room temperature molten salt. This melt was used as the catholyte in the presence of a tungsten cathode on one side of the IONAC separator. The anode compartment again contained an Al anode and $N = 0.37AlCl_3-MEICl$ anolyte.

Cell (b) gave a stable, open-circuit potential of 2.16 V. In order to obtain an estimate of the internal resistance of this cell with its IONAC separator, the current was increased in steps to 0.3 mA, and the stabilized load voltage was then measured in each case. From the slope of a plot of the load voltage *versus* current, Fig. 2, the internal resistance obtained was approximately 6.8×10^3 ohms.

Because of the viscosity of the WCl_6 melt, the cell was warmed to about 40 °C while 0.1 mA of current was passed for about 48 h at load voltages of about 1.5 - 1.0 V. At the end of this time, the tungsten electrode was re-

moved for examination. Within experimental error there was no weight change, and the appearance of the tungsten surface remained the same.

At present, we have no information on the chlorotungstate complex formed when WCl_6 is added to MEICl. Scheffler and Hussey [8] reported that when a small amount of WCl_6 was added to a chloride ion-rich $AlCl_3$–MEICl melt, the chloro-complex WCl_6^- was formed and was accompanied by a one-electron oxidation of the MEICl in the melt. We found that in the case of the 1:2 molar WCl_6–MEICl melt, its ^{13}C nuclear magnetic resonance (NMR) spectrum was analogous to that of molten MEICl itself; whereas a stoichiometric MEICl oxidation would have produced a marked change in the ^{13}C NMR spectrum. Thus, we found no evidence of any oxidation of the MEICl in this binary WCl_6–MEICl melt.

In order to check the effect on the cell voltage of added $AlCl_3$, a melt was prepared by adding 0.997 g of WCl_6 to 3.4315 g of $AlCl_3$–MEICl (N = 0.33) melt. This WCl_6–$AlCl_3$–MEICl melt was used as the anolyte in place of the WCl_6–MEICl melt in cell (b). One beneficial effect was a marked reduction in viscosity of the melt; however, the open-circuit potential was reduced slightly to about 2.14 V. Again, a 0.1 mA current was passed for about 48 h at a load voltage of about 1 V without the tungsten cathode changing its weight within the experimental error.

(ii) Cell without separator
Cell (c)
Al anode/AlBr₃–MEIBr (N = 0.33)/Br₂/RVC, Pt cathode

The anode compartment of this cell, depicted in Fig. 3, consisted of a coil of Al wire in an $AlBr_3$–MEIBr melt (N = 0.33). The cathode compartment consisted of liquid Br_2 in which was immersed a reticulated, vitreous carbon (RVC) current collector which contacted a Pt ring. The Br_2, with
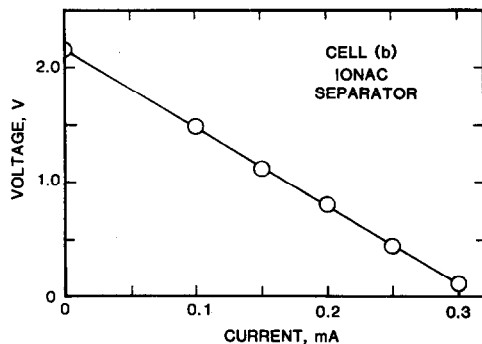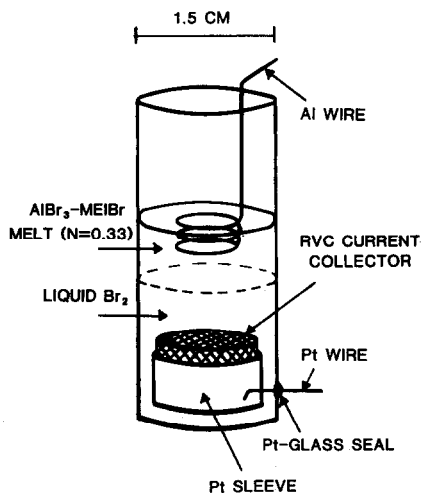

Fig. 2. Voltage/current curve for cell (b).

Fig. 3. Configuration for cell (c).

some of the $N = 0.33$ melt having diffused into it, formed a second, lower phase because of its greater density; therefore no separator was used to separate the anolyte and catholyte.

The open-circuit potential of this cell was 2.19 V and it was discharged at a 1 mA current for 1 day at 1.7 V. During this time, the phase boundary gradually moved toward the Al anode, until a violent reaction occurred when the Al wire touched the bromine-rich phase.

The expected anode, cathode, and cell reactions are:

anode: $Al + 4Br^- \longrightarrow AlBr_4^- + 3e^-$ (9)

cathode: $3/2Br_2 + 3e^- \longrightarrow 3Br^-$ (10)

cell: $Al + 3/2Br_2 + Br^- \longrightarrow AlBr_4^-$ (11)

The cell reaction shows the Br_2 in the cathode compartment being converted to Br^-. The expansion of the lower phase is probably due to continued slow dissolution of the heavier bromine-rich phase in the upper melt phase.

The theoretical specific energy of the electroactive materials for cell reaction (11) is 510 W h/kg, which makes this cell attractive for battery use, but a separator is needed which will restrict Br_2 to the cathode compartment. As long as a basic melt is used in the anode compartment, this cell will not be rechargeable. An acidic melt can be used as the anolyte, but this will lower the open-circuit voltage to approximately 1 V, and will result in a proportionately lower specific energy for the cell. Also, unpublished results from this laboratory have shown that bromination of the carbon–carbon double bond in the MEI^+ occurs in acidic melts.

(iii) Cells using NAFION® separators

Cell (d)

Zn anode/AlCl₃–MEICl (N = 0.33)//AlCl₃–MEICl (N = 0.60)/Al cathode

A cell of this form was obtained by charging a cell in which the 0.33 melt contained 20% by weight of anhydrous zinc chloride which was in contact with a tungsten foil electrode so that the zinc was plated onto the tungsten, the initial form of the cell being:

$W/ZnCl_2$ (20% by wt.) in $AlCl_3$–MEICl ($N = 0.33$)//$AlCl_3$–MEICl
($N = 0.60$)/Al

The charging current was a constant 0.5 mA for 17.6 h and the open-circuit potential for the charged cell was 0.73 V. The cell was discharged at constant currents of 0.5 mA for 8.5 h and 0.2 mA for 17.2 h. At the end of this time the cell showed complete discharge. The number of coulombs discharged (27.7) was approximately 87% of the number of coulombs passed during the charging of the cell (31.7).

The cell was recharged with 1 mA current at 0.9 - 1.0 V for about 24 h. The charging potential then increased steeply to 2.2 V and remained at this level (see Fig. 4). The 2.2 V portion of the charge curve is probably due to decomposition of the melt by reduction of the imidazolium cation as the
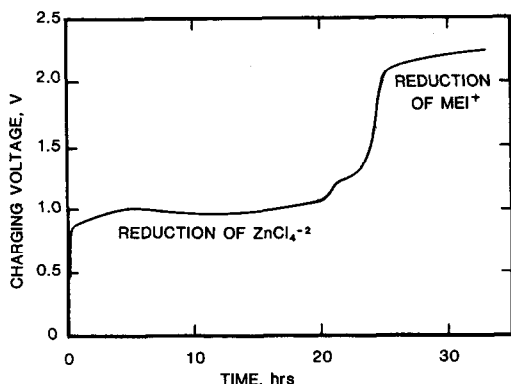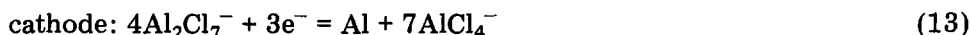
Fig. 4. Charging curve for cell (d). A constant charging current of 1.0 mA was used.

dissolved zinc chloride complex concentration becomes very small. The evidence for reduction of the melt was the appearance of the deep orange color that typifies the reduction of the imidazolium ion in basic melts. Examination of the anode of this cell after recharging showed evidence of metallic zinc adhering in granular chunks to the tungsten surface.

The probable anode, cathode, and cell reactions are:

anode: $Zn + 4Cl^- = ZnCl_4{}^{2-} + 2e^-$ (12)

cathode: $4Al_2Cl_7{}^- + 3e^- = Al + 7AlCl_4{}^-$ (13)

cell: $3/2Zn + 4Al_2Cl_7{}^- + 6Cl^- = 3/2ZnCl_4{}^{2-} + Al + 7AlCl_4{}^-$ (14)

The theoretical specific energy of the electroactive materials for a cell based on cell reaction (14) is 37 W h/kg. This value is low because of the low cell voltage and the large molecular weights of the electroactives involved in the cell reaction.

Cell (e)
Cd anode/AlCl$_3$–MEICl (N = 0.33)//AlCl$_3$–MEICl (N = 0.60)/Al cathode
As in the case of the zinc anode (d), the anode in this cell was obtained by plating the cadmium metal onto tungsten from the appropriate metal halide in the anolyte compartment. The initial form of the cell was:

W/CdCl$_2$ (20% by wt.) in AlCl$_3$–MEICl ($N = 0.33$)//AlCl$_3$–MEICl
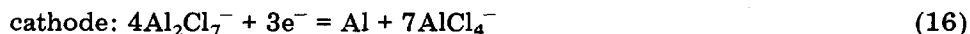$$(N = 0.60)/Al$$

The charging current was 0.5 mA at about 1.22 V and the open-circuit potential of the charged cell, after the initial charge of 36.9 coulombs, was about 1.1 V.

In order to test the reversibility of the above Al/Cd cell it was cycled through charge and discharge five times with the end of discharge being when the voltage dropped abruptly. The charge/discharge efficiency varied from 43% to 67%, with the largest value occurring for the last cycle. An

examination of the anode after a final charge showed evidence of metallic cadmium adhering to the tungsten foil.

While all the electrochemical data for the above cell are approximate values for a first test of an Al/Cd molten salt cell, we have been able to show that this cell can be reversibly cycled. From a review of the literature, this appears to be the first demonstration of the operation of a secondary room temperature molten salt electrochemical cell.

The probable anode, cathode and cell reactions are:

anode: $Cd + 4Cl^- = CdCl_4^{2-} + 2e^-$ (15)

cathode: $4Al_2Cl_7^- + 3e^- = Al + 7AlCl_4^-$ (16)

cell: $3/2Cd + 4Al_2Cl_7^- + 6Cl^- = 3/2CdCl_4^{2-} + Al + 7AlCl_4^-$ (17)

An additional experiment was performed to test whether the anode reaction was that shown in eqn. (15). Cadmium foil was used in place of the tungsten electrode and the cell was discharged with 1.54 equivalents of charge passed. The mass loss of Cd was measured as within 4% of the value calculated from eqn. (15).

Cell reaction (17) corresponds to a theoretical specific energy of the electroactive materials for this cell of about 66 W h/kg-electroactives. This specific energy is an improvement over cell (d) because of the increased voltage of the Al/Cd cell.

(iv) Half-cell reduction potentials in room temperature molten salts

The potential measurements obtained for the various cell combinations studied in this work can be used to obtain relative values of half-cell reduction potentials in the 1-methyl-3-ethylimidazolium chloride room temperature molten salts. Table 1 shows such potentials in which the reversible Al/AlCl$_3$–MEICl ($N = 0.60$) electrode has been chosen as the reference electrode and assigned a half-cell reduction potential of 0.0 V. As a test of whether this Table can be used to predict cell potentials from a combination

TABLE 1

Molten salt half-cell potentials using as reference $N = 0.60$ Al/AlCl$_3$–MEICl

	Potential (V)
Br$_2$ ($N = 0.33$ AlBr$_3$–MEIBr) + 2e$^-$ = 2Br$^-$	+0.81
W^{m+} ($N = 0.33$ WCl$_6$–MEICl) + ne$^-$ = W$^{(m-n)+}$	+0.78
W^{m+} (20 wt.% WCl$_6$ in $N = 0.33$ AlCl$_3$–MEICl) + ne$^-$ = W$^{(m-n)+}$	+0.76
Fe^{3+} ($N = 0.33$ FeCl$_3$–MEICl) + e$^-$ = Fe^{2+}	+0.37
Al^{3+} ($N = 0.60$ AlCl$_3$–MEICl) + 3e$^-$ = Al	+0.00
Cu$^+$ ($N = 0.24$ CuCl–MEICl) + e$^-$ = Cu	−0.51
Zn^{2+} (20 wt.% ZnCl$_2$ in $N = 0.33$ AlCl$_3$–MEICl) + 2e$^-$ = Zn	−0.73
Cd^{2+} (20 wt.% CdCl$_2$ in $N = 0.33$ AlCl$_3$–MEICl) + 2e$^-$ = Cd	−0.96
Al^{3+} ($N = 0.37$ AlCl$_3$–MEICl) + 3e$^-$ = Al	−1.38

of half-cell potentials, e.m.f. measurements were made on the following Al/Cd cells (1) and (2), in which the Cd/CdCl$_2$ half-cell was combined with the Al electrode immersed in $N = 0.60$ and $N = 0.37$ AlCl$_3$–MEICl melts, respectively:

(1) Cd anode/CdCl$_2$ (20% by wt. in $N = 0.33$ AlCl$_3$–MEICl)//AlCl$_3$–MEICl

$$(N = 0.60)/\text{Al}$$

(2) Al anode/AlCl$_3$–MEICl ($N = 0.37$)//CdCl$_2$ (20% by wt. in $N = 0.37$

$$\text{AlCl}_3\text{–MEICl})/\text{Al}$$

The open-circuit potentials for cells (1) and (2) were about 1.01 V and 0.43 V, respectively. Combination of cells (1) and (2) gives an approximate value (approximate, since the CdCl$_2$ was dissolved in $N = 0.33$ melt in cell (1) and $N = 0.37$ melt in cell (2)) of -1.4 V for the reduction potential of the Al/AlCl$_3$–MEICl ($N = 0.37$) half-cell *vs.* the reference. This is in good agreement with the reported value [6] of -1.38 V for this half-cell compared with the reference half-cell.

E.m.f. measurements were also made on the Al/Cu cells (3) and (4), in which the Cu/CuCl–MEICl ($N = 0.24$) half-cell was combined with the Al electrode immersed in $N = 0.60$ and $N = 0.37$ AlCl$_3$–MEICl melts, respectively:

(3) Cu anode/CuCl–MEICl ($N = 0.24$)//AlCl$_3$–MEICl ($N = 0.60$)/Al cathode

(4) Al anode/AlCl$_3$–MEICl ($N = 0.37$)//CuCl–MEICl ($N = 0.24$)/Cu cathode

The open-circuit potentials for cells (3) and (4) were about 0.51 V and 0.79 V, respectively. Combination of cells (3) and (4) gives about -1.3 V for the reduction potential of the Al/AlCl$_3$–MEICl ($N = 0.37$) half-cell *vs.* the reference. This is in fair agreement with the reported value [6] of -1.38 V.

An important point to note about the half-cell reactions listed in Table 1 is that while the cations are shown for simplicity, as uncomplexed, these cations in the basic melts are present as the chloro complexes. It should also be pointed out that the half-cell reduction potentials for the zinc and cadmium electrodes are in reverse order in the molten salt from that in aqueous solution. This result indicates an increased stability of the cadmium chloride complex in the 1-methyl-3-ethylimidazolium chloride molten salts compared with the zinc chloride complex.

Conclusion

Three new primary cells were examined using room temperature molten salt electrolytes. Compared with the Al/AlCl$_3$–MEICl concentration cell, these primary cells had relatively high open-circuit potentials in the range 1.75 - 2.19 V.

Two new secondary electrochemical cell candidates were examined which combined the reversible Al/AlCl$_3$–MEICl (N = 0.60) electrode with reversible zinc and cadmium molten salt electrodes to give open-circuit potentials of about 0.7 and 1.0 V, respectively. The secondary cadmium cell was cycled through charge and discharge five times, with efficiencies up to 65%.

A Table of half-cell reduction potentials in room temperature molten salts has been presented. These reduction potentials can be combined to give approximate values of cell potentials for various electrochemical cells.

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